The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

Workshop on "Physics for Renewable Energy"
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"Hydrogen Storage for Transportation & other Applications"

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Hydrogen storage for transportation..
… and other applications.

Pier Paolo Prosini

ENEA – Hydrogen and Fuel Cell Project

Origin of the Earth's Atmosphere

- Early Earth would have been very different and inhospitable compared to the Earth today.
- Hot

  - ➔ *Why?* - Primordial heat, collisions and compression during accretion, decay of short-lived radioactive elements
  - ➔ *Consequences* - Constant volcanism, surface temperature too high for liquid water or life as we know it, molten surface or thin, unstable basaltic crust.
- Atmosphere - early atmosphere probably completely different in composition (H2, He)

Evolution of the Atmosphere

- Cooling

Primordial heat dissipated to space.

Condensation of water (rain), accumulation of surface water.

Accumulation of new atmosphere due to volcanic out gassing.

Conditions appropriate for evolution of life.

Atmosphere

- Envelope of gases that surrounds the Earth. Used by life as a reservoir of chemical compounds used in living systems. Atmosphere has no outer boundary, just fades into space. Dense part of atmosphere (97% of mass) lies within 30 km of the Earth (so about same thickness as continental crust).

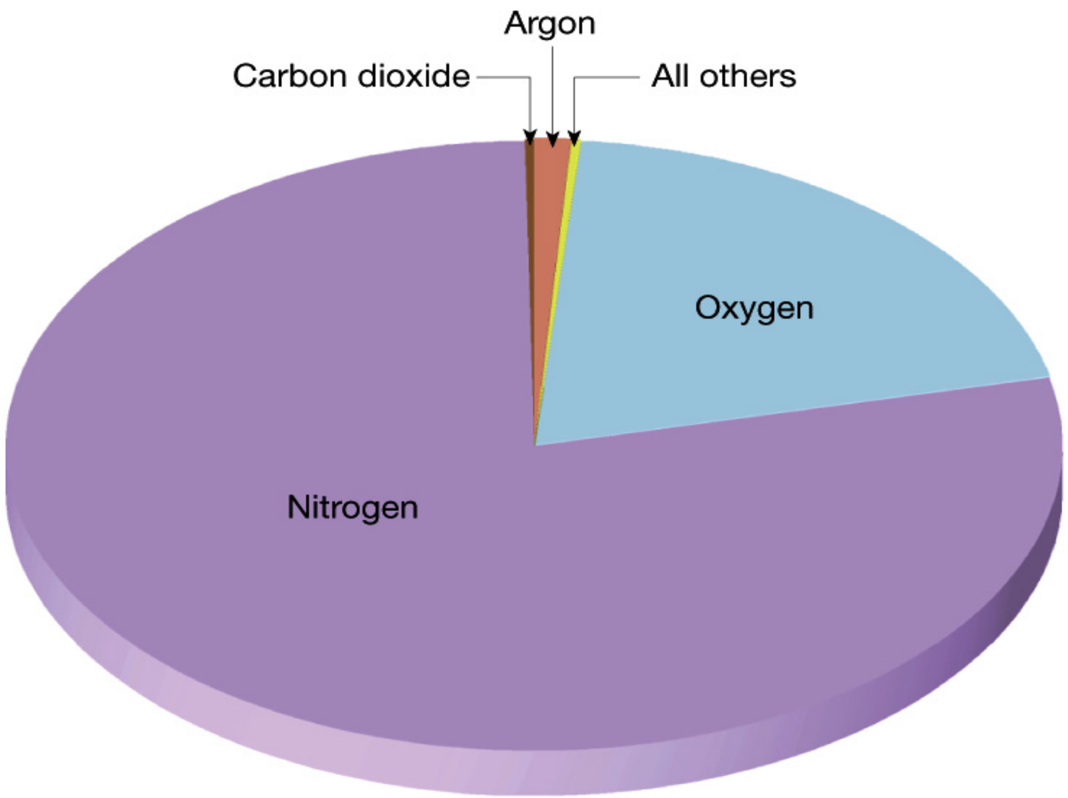


figure from Lutgens and Tarbuck, *The Atmosphere*, 8th edition

First Atmosphere

- Composition - Probably H_2, He
- These gases are relatively rare on Earth compared to other places in the universe and were probably lost to space early in Earth's history because
  - ➔ Earth's gravity is not strong enough to hold lighter gases
  - ➔ Earth still did not have a differentiated core (solid inner/liquid outer core) which creates Earth's magnetic field (magnetosphere = Van Allen Belt) which deflects solar winds.
- Once the core differentiated the heavier gases could be retained

Second Atmosphere

- Produced by *volcanic out gassing.*

- Gases produced were probably similar to those created by modern volcanoes (H_2O, CO_2, SO_2, CO, S_2, Cl_2, N_2, H_2) and NH_3 (ammonia) and CH_4 (methane)
- No free O_2 at this time (not found in volcanic gases).
- *Ocean Formation* - As the Earth cooled, H_2O produced by out gassing could exist as liquid in the Early Archean, allowing oceans to form.
  - ➔ Evidence - pillow basalts, deep marine seds in greenstone belts.

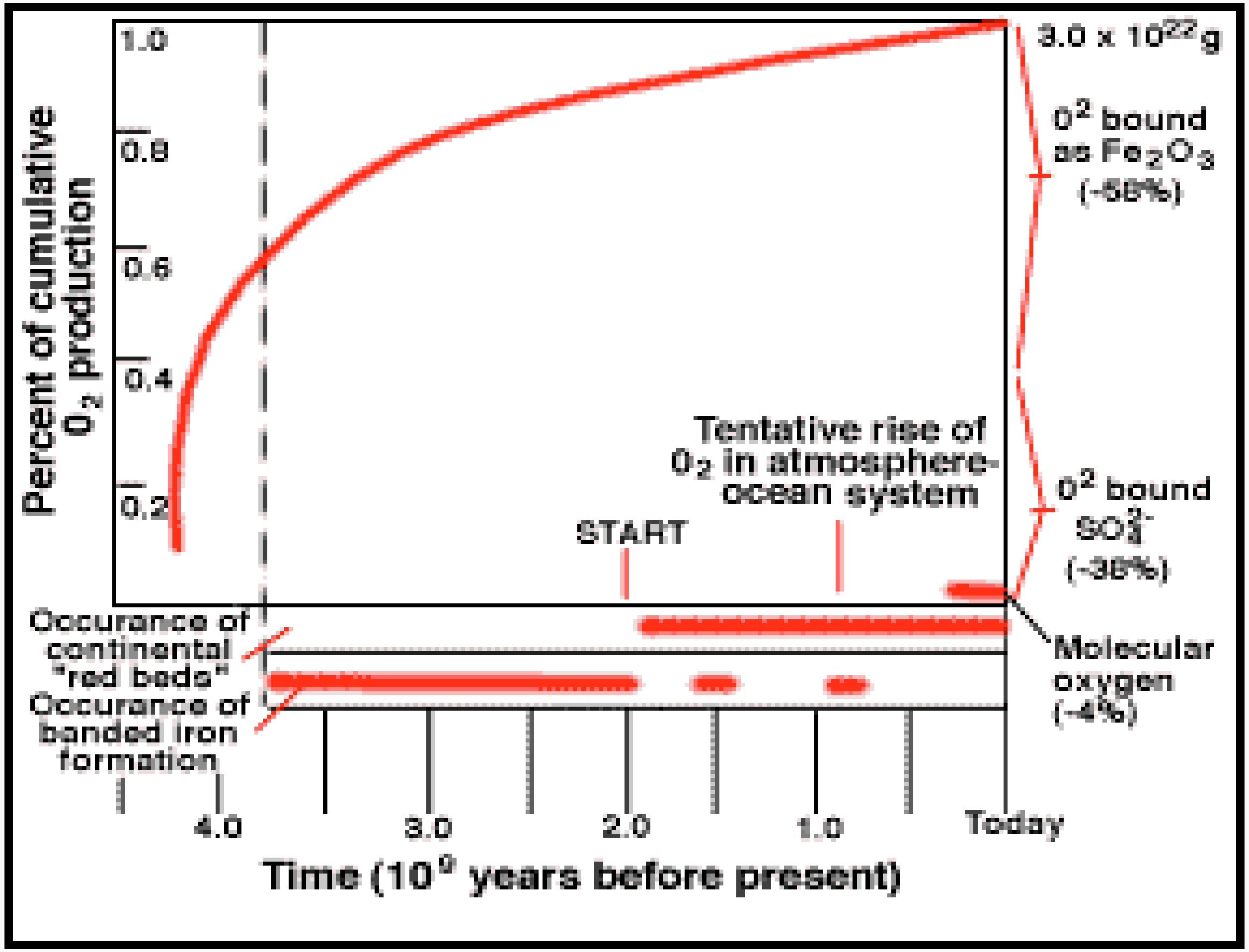
Addition of O_2 to the Atmosphere

- Today, the atmosphere is ~21% free oxygen (about $1.5x10^{15}$ tons). How did oxygen reach these levels in the atmosphere? Revisit the oxygen cycle:
- **Oxygen Production**
  - **Photochemical dissociation** - breakup of water molecules by ultraviolet
    - Produced O_2 levels approx. 1-2% current levels
    - At these levels O_3 (Ozone) can form to shield Earth surface from UV
  - **Photosynthesis** - CO_2 + H_2O + sunlight = organic compounds + O_2 - produced by cyanobacteria, and eventually higher plants - supplied the rest of O2 to atmosphere. Thus plant populations

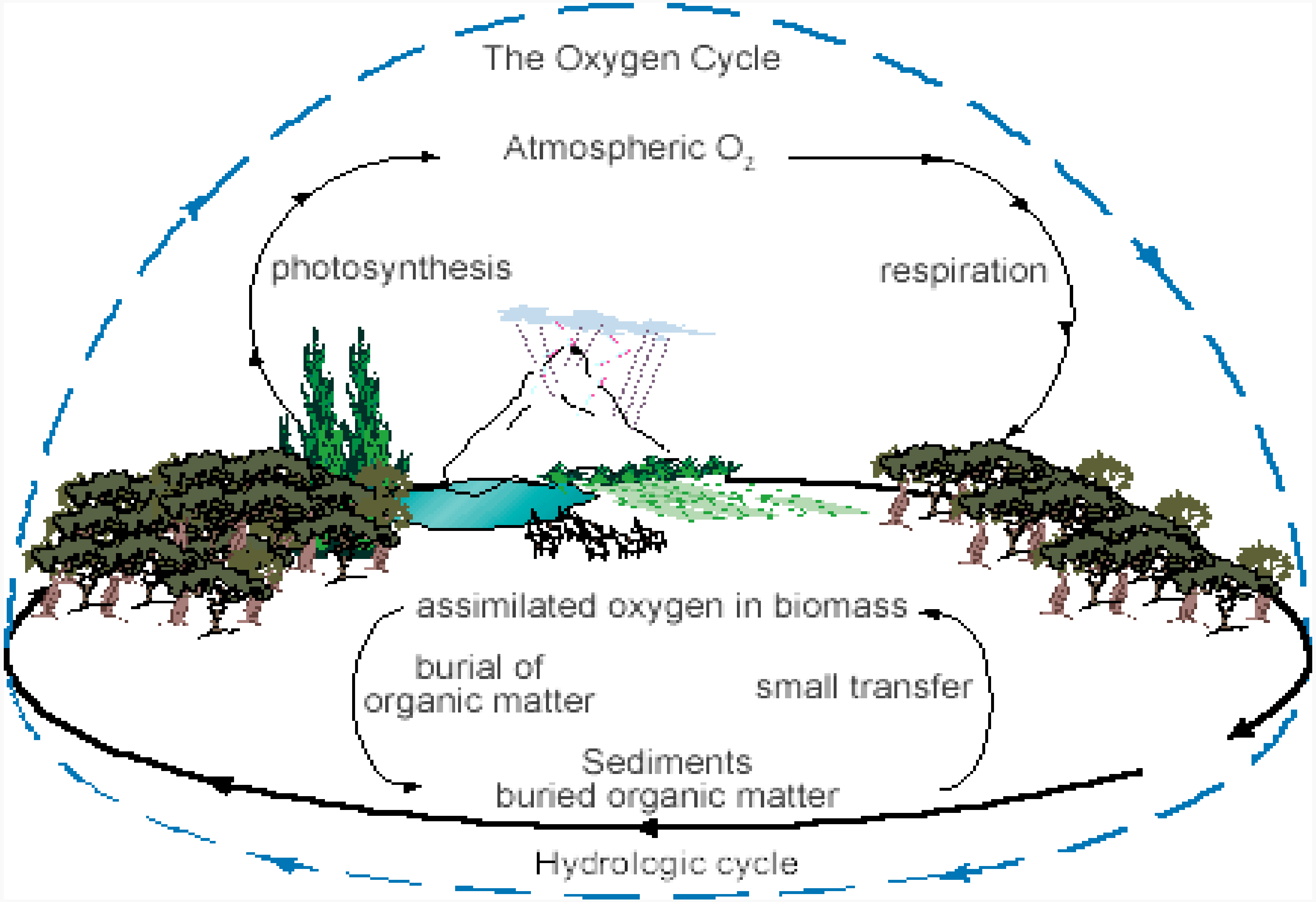
Evidence from the Rock Record

- Iron (Fe) is extremely reactive with oxygen. If we look at the oxidation state of Fe in the rock record, we can infer a great deal about atmospheric evolution.
- **Archean** - Find occurrence of minerals that only form in non-oxidizing environments in Archean sediments: Pyrite (Fools gold; FeS_2), Uraninite (UO_2). These minerals are easily dissolved out of rocks under present atmospheric conditions.
- ***Banded Iron Formation (BIF)*** - Deep water deposits in which layers of iron-rich minerals alternate with iron-poor layers, primarily chert. Iron minerals include iron oxide, iron carbonate, iron silicate, iron sulfide. BIF's are a major source of iron ore, b/c they contain magnetite (Fe_3O_4) which has a higher iron-to-oxygen ratio than hematite. These are common in rocks 2.0 - 2.8 B.y. old, but do not form today.
- ***Red beds*** (continental siliciclastic deposits) are never found in rocks older than 2.3 B. y., but are common during Phanerozoic time. Red beds are red because of the highly oxidized mineral hematite (Fe_2O_3), that probably forms secondarily by oxidation of other Fe minerals that have accumulated in the sediment.

Conclusion:
The amount of O_2 in the atmosphere has increased with time.



The Oxygen Cycle



How many energy is stored in our earth ?

- If we think that one mol of carbon-equivalent has been produced for each mol of oxygen:

$$CO_2 \longrightarrow C + O_2$$

- The amount of energy stored in the earth is very impressive.
- The total amount of oxygen is evaluated to be 3×10^{16} tons that corresponds to 1×10^{16} tons of carbon-equivalent.

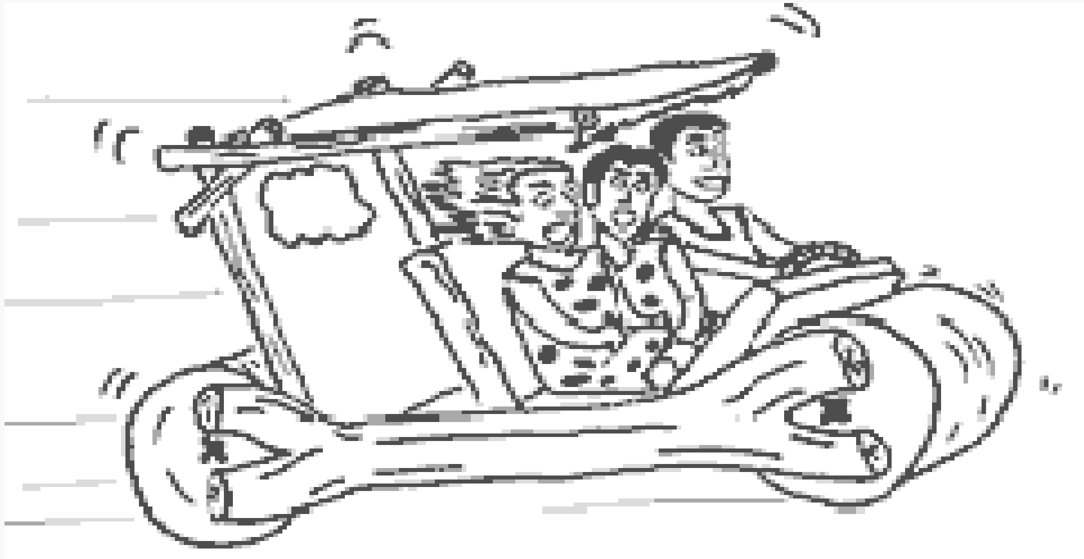
How far is your horizon ?

- Today we extract about $3x10^9$ of tons of oil per year.
- Burning the oil at this rate it will decrease the oxygen content of the atmosphere from 20.95% to 19.95% in **about 24,000 years.**
- In that time the quantity of carbon-equivalent burned will represent 0.72 % of the total reserve.

How far is my horizon ?

- The estimated amount of oil is about $9x10^{10}$ milliards of tons.
- Oil will finished in about 30-40 years

How we can move without gasoline?



Hydrocarbons represent the only valid way to power automobiles.

◆ The energy content of gasoline is very impressive:

- The Energy Density by volume is 8.76 kWh/l
- The Energy Density by weight is 12.7 kWh/kg

➔ A “full” of gasoline for a medium power car is about 40 liter:

- The energy content of a gasoline tank is 350 kWh
- Only 15% of the energy is used to power the vehicle
- About 300kW are dispersed as heat

The negative impact:
Hydrocarbons are very polluting agents.

- The prospective of sharing another decade with hydrocarbon combustion products from automobile engines

IS NOT ACCEPTABLE !

General criteria for the design and selection of on-board storage systems

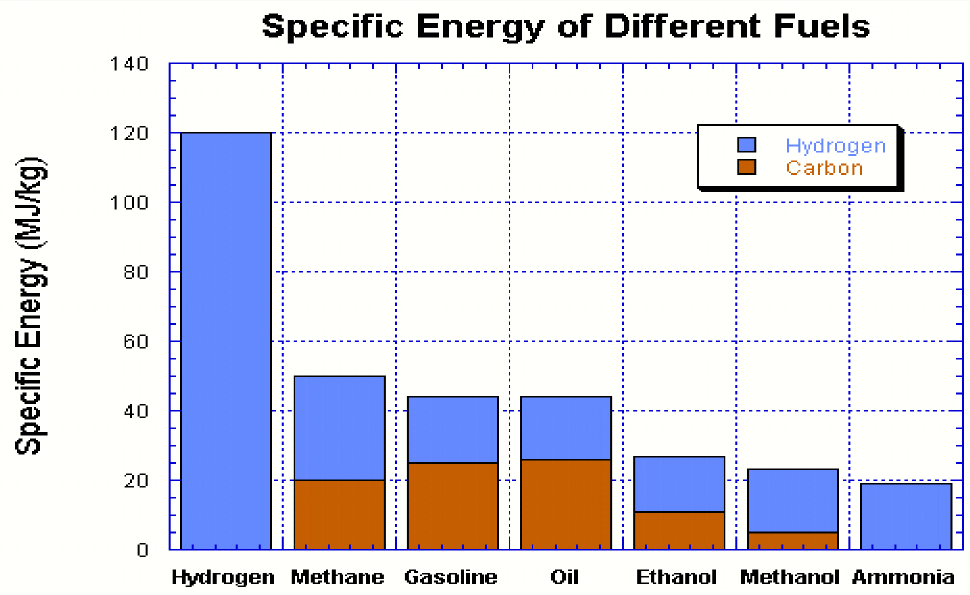
EXTERNAL FACTORS

- Transport and distribution infrastructure
- Interface between distribution network and end users
- Codes and standards

INTERNAL FACTORS

- Specific energy and power properties: weight and volume
- Working operating conditions
- Efficiency: charge/discharge and self-discharge
- Operating and investment costs
- Safety use of components and large availability

THERE WILL BE HYDROGEN IN OUR FUTURE ?

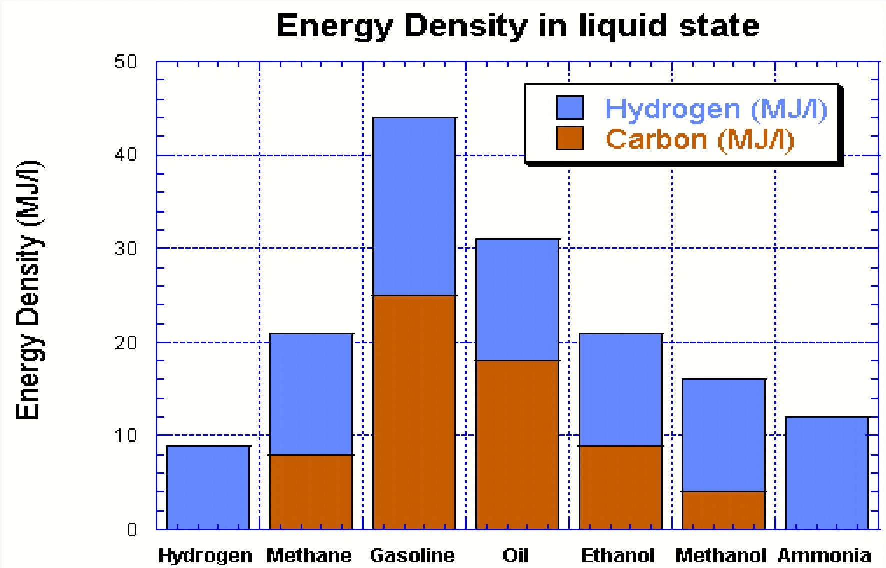


Hydrogen has the highest energy mass density:

120 MJ/kg (LHV)

144 MJ/kg (HHV)

Unfortunately 1 litre of hydrogen @ 1 bar and RT contains only: **10.7 kJ**



Technical specifications for On-board Hydrogen Storage Systems

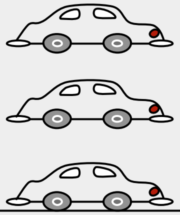
Main Barriers are Weight, Volume, Cost, and Refueling Time

What do these targets mean? For a 5-kg H_2 system…

Storage Parameter	2005	2010	2015
Gravimetric Capacity (Specific energy)	1.5 kWh/kg 0.045 kg H_2/kg	2.0 kWh/kg 0.060 kg H_2/kg	3.0 kWh/kg 0.090 kg H_2/kg
System Weight:	***111 Kg***	***83 Kg***	***55.6 Kg***
Volumetric Capacity (Energy density)	1.2 kWh/L 0.036 kg H_2/L	1.5 kWh/L 0.045 kg H_2/L	2.7 kWh/L 0.081 kg H_2/L
System Volume:	***139 L***	***111 L***	***62 L***
Storage system cost	$6 /kWh	$4 /kWh	$2 /kWh
System Cost:	***$1000***	***$666***	***$333***
Refueling rate	.5 Kg H_2/min	1.5 Kg H_2/min	2.0 Kg H_2/min
Refueling Time:	***10 min***	***3.3 min***	***2.5 min***

How large of a gas tank do you want?

Storage remains a problem!



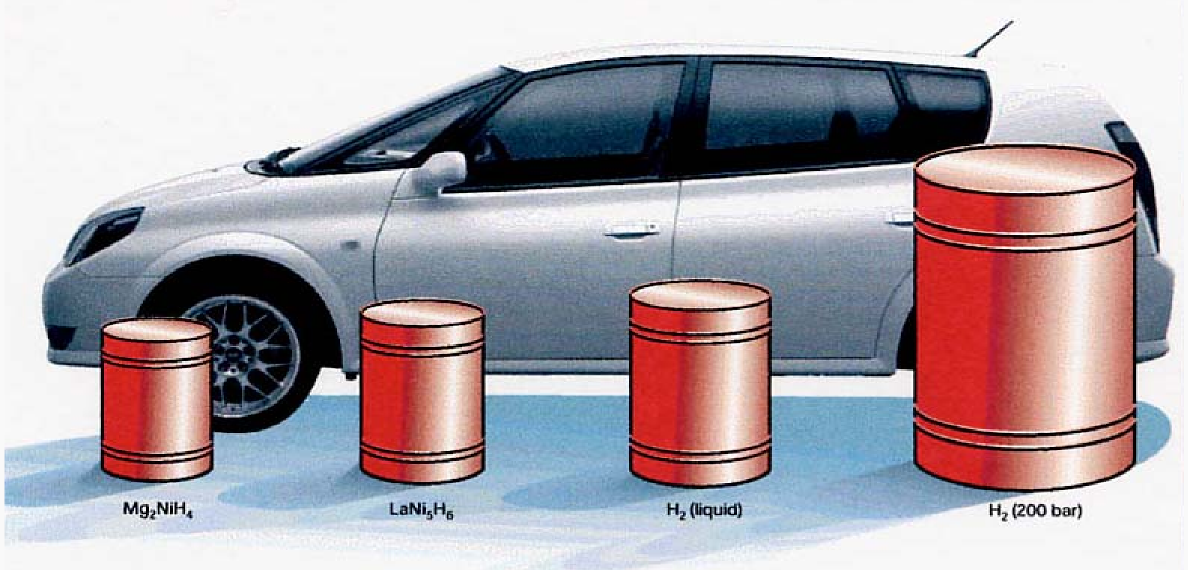
Electric car with fuel cell (4kg H)

Combustion engine (8kg H)

Combustion engine (24 kg petrol)

400 km

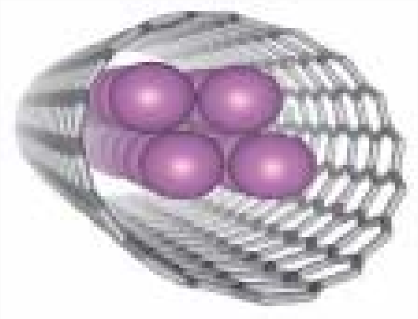
Volume Comparisons for 4 kg Vehicular H_2 Storage



Schlapbach & Züttel, Nature, 15 Nov. 2001

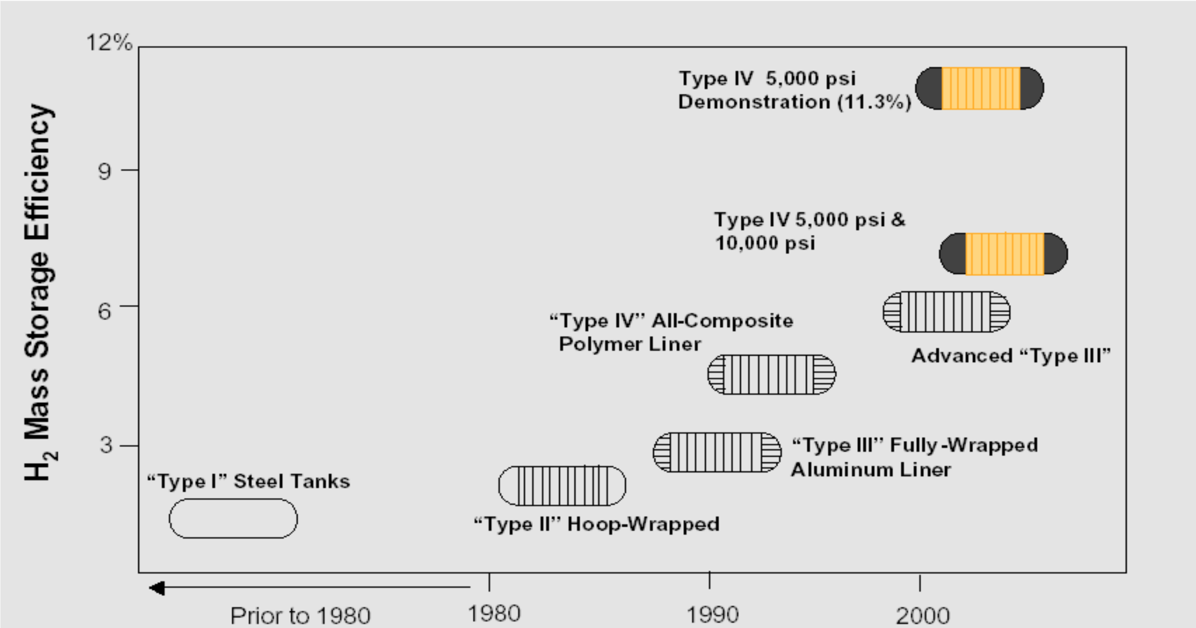
Hydrogen storage alternatives

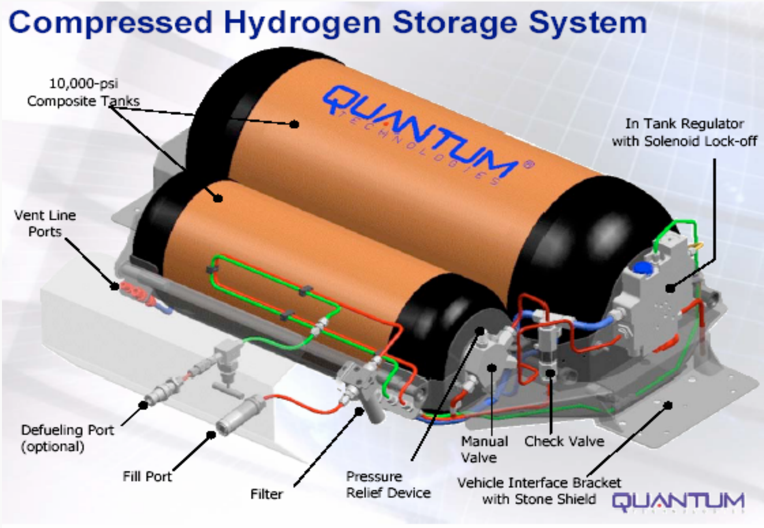
- **Conventional systems**
  - ➔ Hydrogen gas in pressurised tanks (conformable)
  - ➔ Liquid in cryogenic tanks (dewar)
- **Advanced storage (direct or indirect)**
  - ➔ Hydrides (reversible and irreversible)



Compressed Gas Tank

11-13 w% achieved
Quantum and GM certified 700 bar tank.
Codes and standards are still an issue.
Commercial.



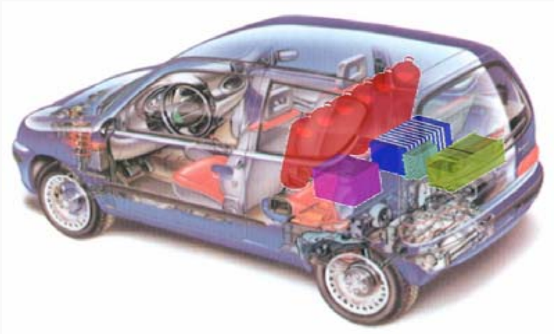


Compressed Gas Tank: still open issues

Safety

- Car accident case
- Car fire case
- During re-fuelling

Space problems



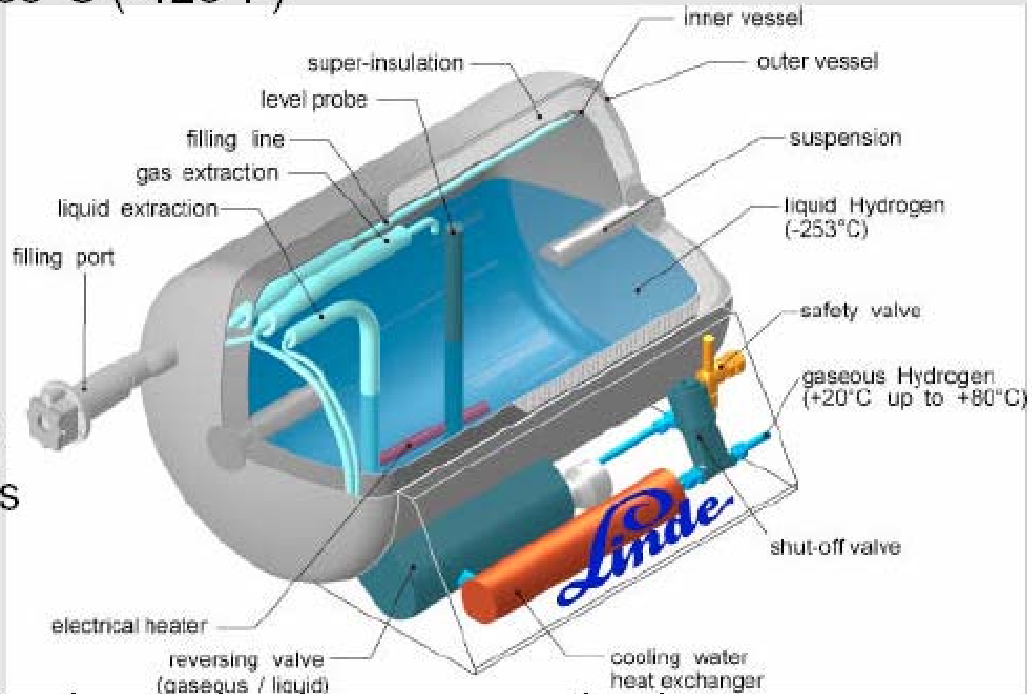
An integrated project required

FIAT 600 FC

Traditional and conformable tank

Liquid Hydrogen Storage

- Cryogenic storage of hydrogen @ -253°C (-423°F)
- Advantages
  - Low pressure
  - High storage density
- Disadvantages
  - Energy required for liquefaction
  - Evaporative losses during fueling
  - Evaporative losses during periods of inactivity, i.e. when parked
  - Consumer Acceptance

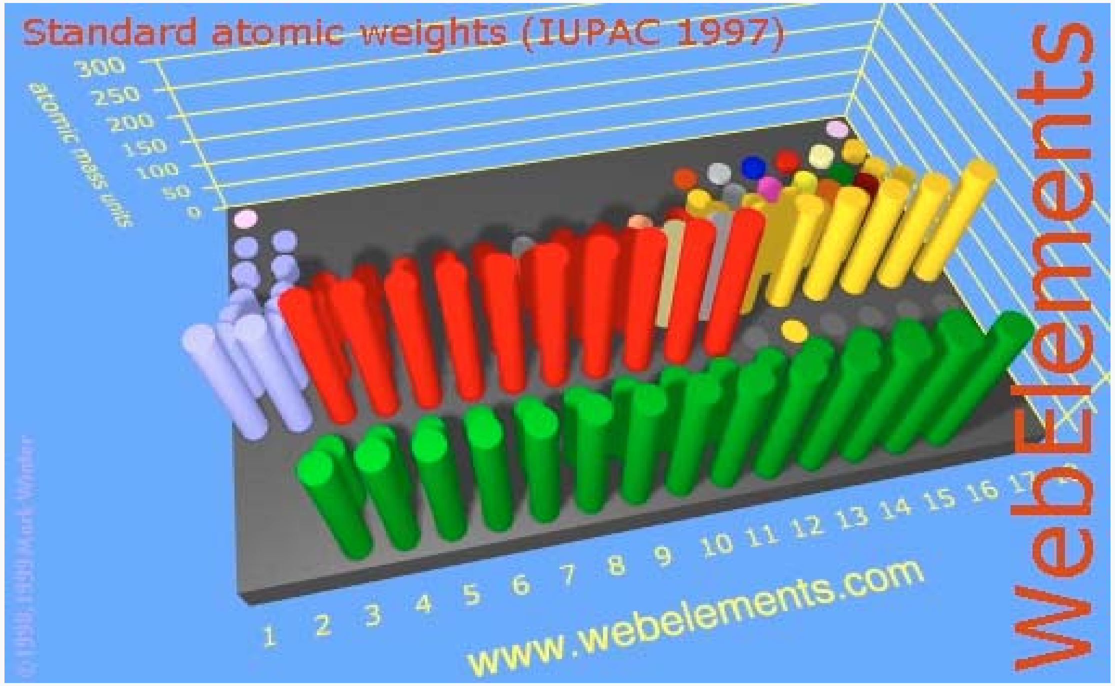


- Future developments to improve packaging and reduce evaporative losses
  - Linde AG
  - Lawrence Livermore National Laboratory

Solid metal hydride

To meet DOE goals a metal hydride should have:

1. Low molecular weight and/or high hydrogen content
2. High density
3. Low reaction enthalpy
4. Low cost



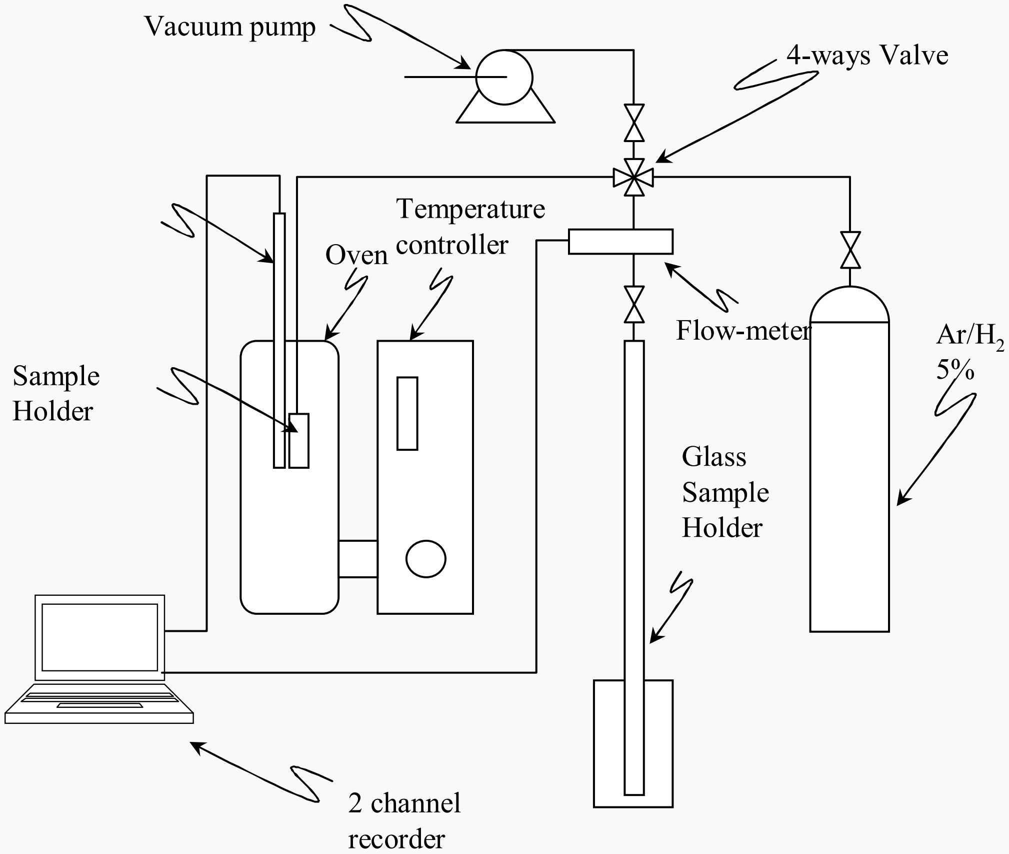
ENEA MEDIUM TERM ACTIVITIES (2006): $NaAlH_4$

- $3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2$ 3.7% wt. H_2
- $Na_3AlH_6 \longrightarrow 3NaH + Al + 3/2H_2$ 1.85% wt. H_2

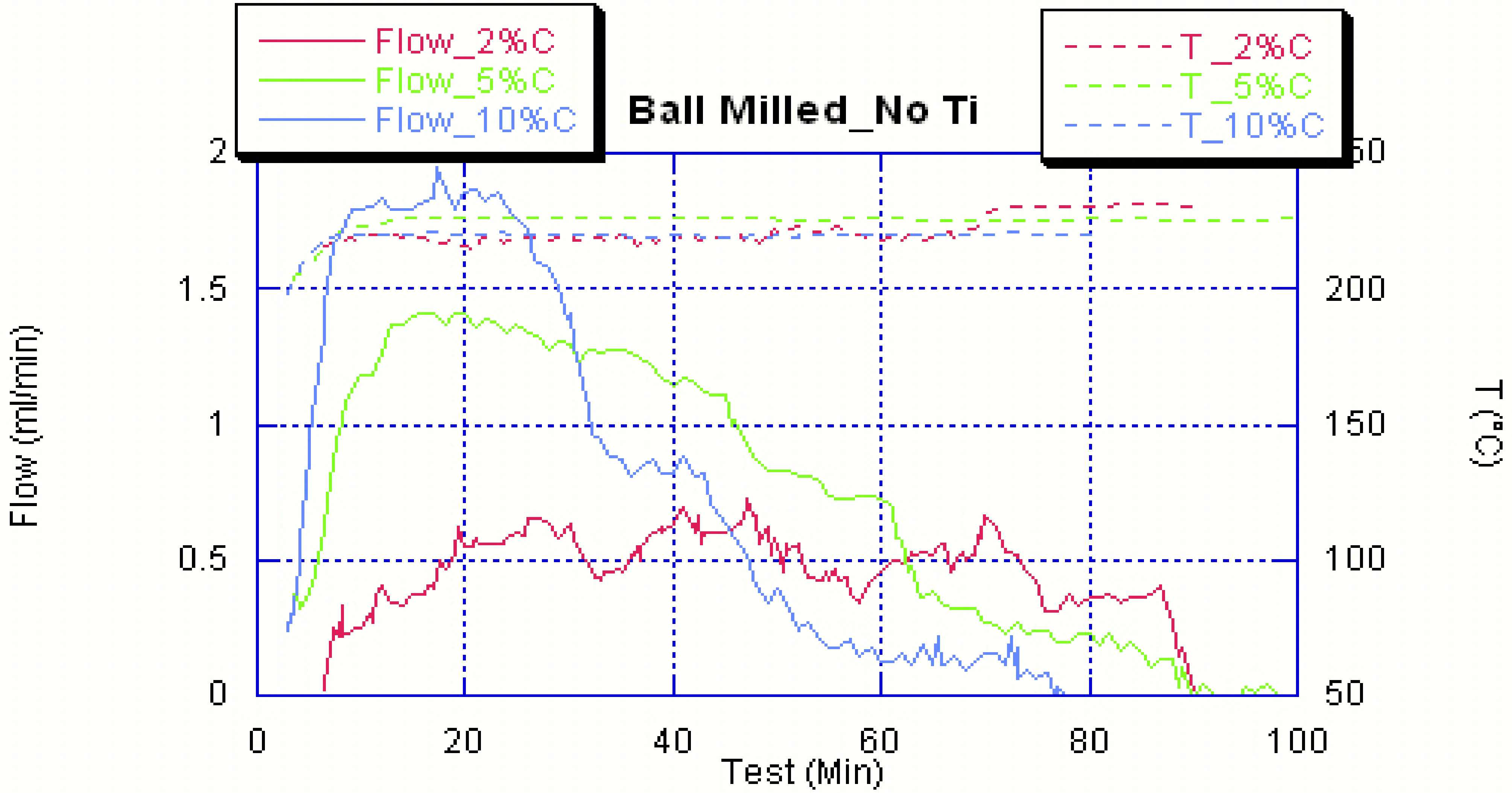
- RESEARCH ACTIVITIES HAVE BEEN FOCUSED ON:

- 1. THE EFFECT OF HIGH SURFACE AREA ADDITIVES (CARBON)
- 2. THE INCREDIBLE ACTIVATION OF TITANIUM

ATM. PRESSURE FACILITY FOR H_2 DESORPTION



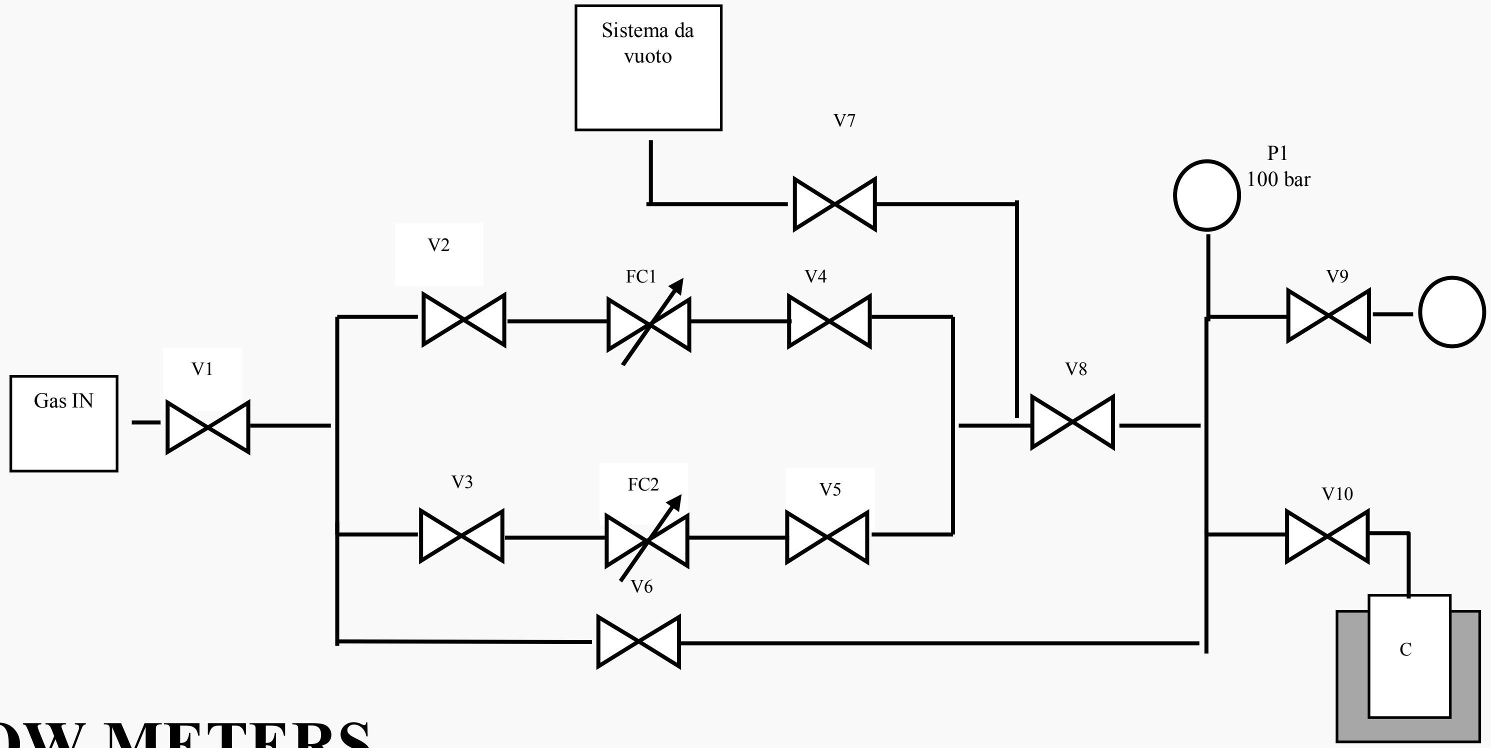
THE EFFECT OF THE CARBON



PCI FEATURES

- Temperature: R.T. up to 500°C
- Pressure: 0.01 bar up to 80 bar
- Flow: 1 ml/min up to 500 ml/min

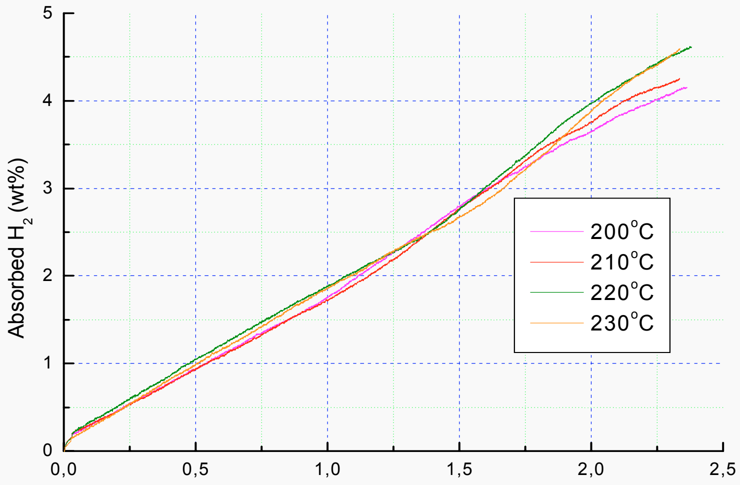
TWO PRESSURE GAUGES



TWO FLOW METERS

THE PCI SYSTEM

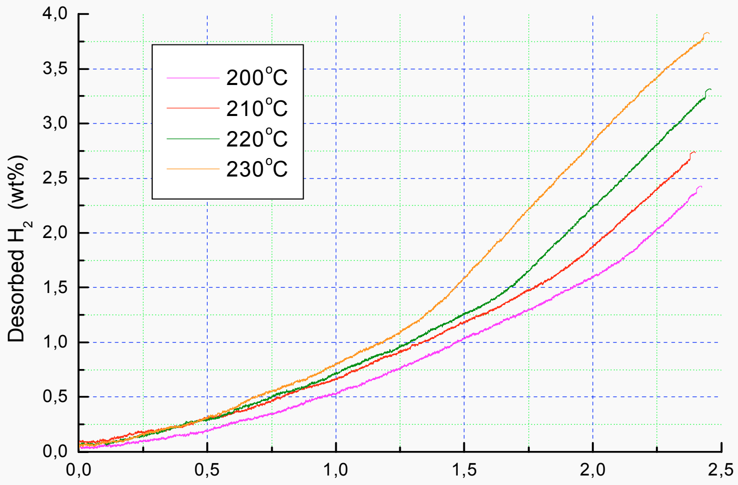
PCI CURVES ON CARBON MIXED $NaAlH_4$



NaAlH4 + 10wt% Carbon:
Pmax=80bar, Flow=40nccm/min, Pgas in=81bar

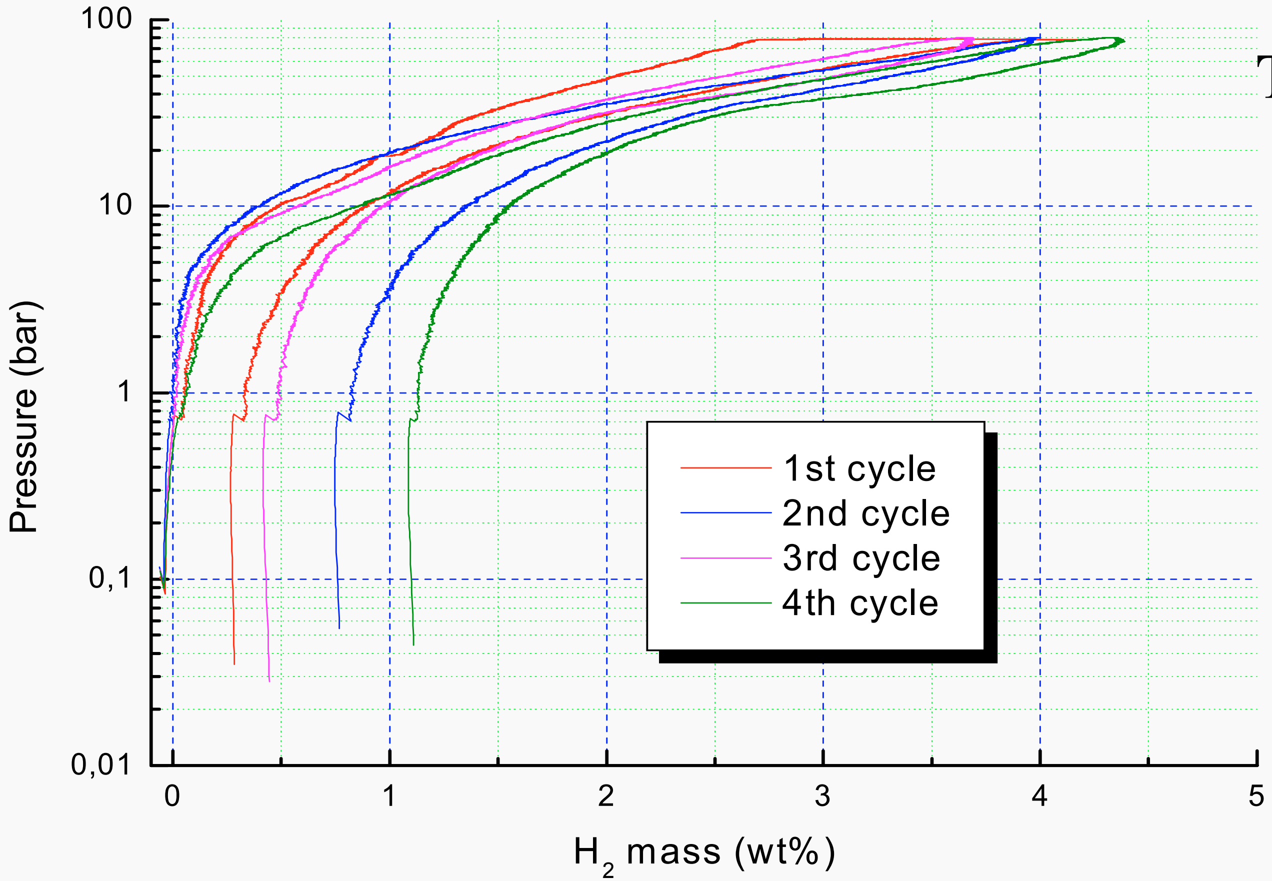
Hydrogen absorption was almost independent on temperature

Larger hydrogen contents were released by increasing temperature



NaAlH4 + 10wt% Carbon:
Pmax=80bar, Flow=40nccm/min, Pgas in=81bar

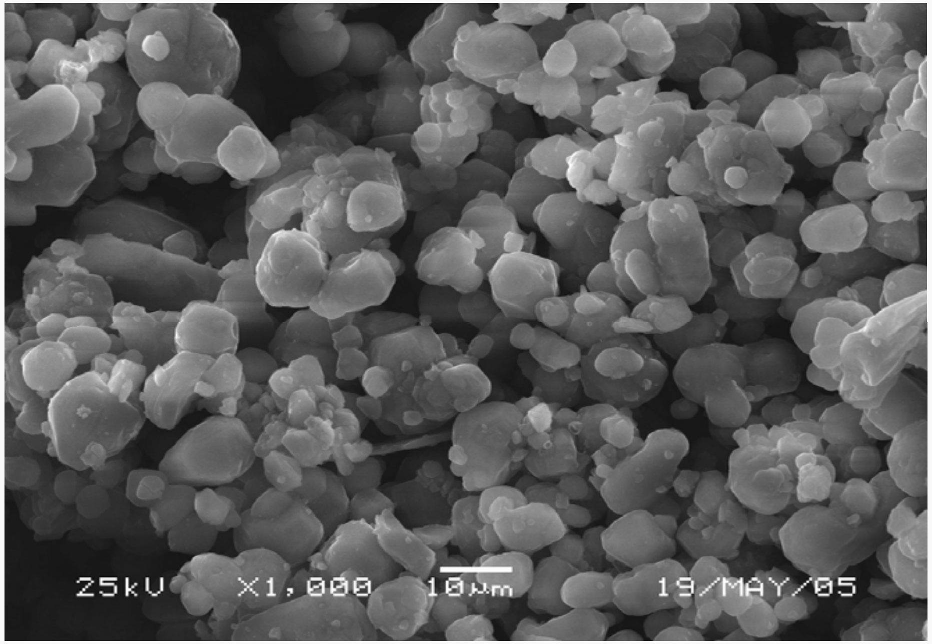
CYCLING TITANIUM DOPED $NaAlH_4$



T = 140°C

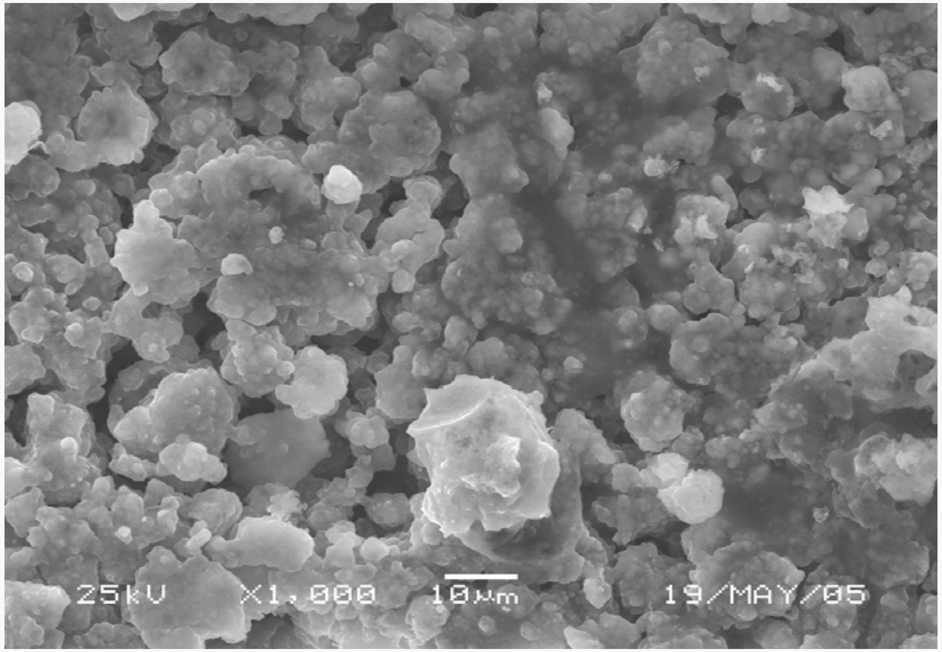
$NaAlH_4$+Ti P_{max}=80bar, Flow=40nccm/min, Temp=140°C, $P_{gas\ in}$=81bar

MORPHOLOGICAL MODIFICATIONS

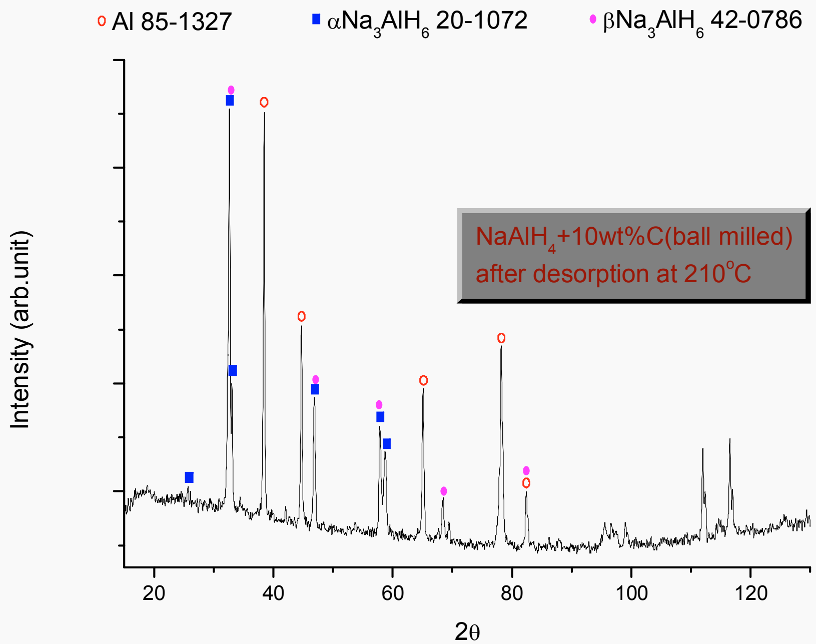


Doped Ti-NaAlH4 before dehydrogenation…

……..and after dehydrogenation

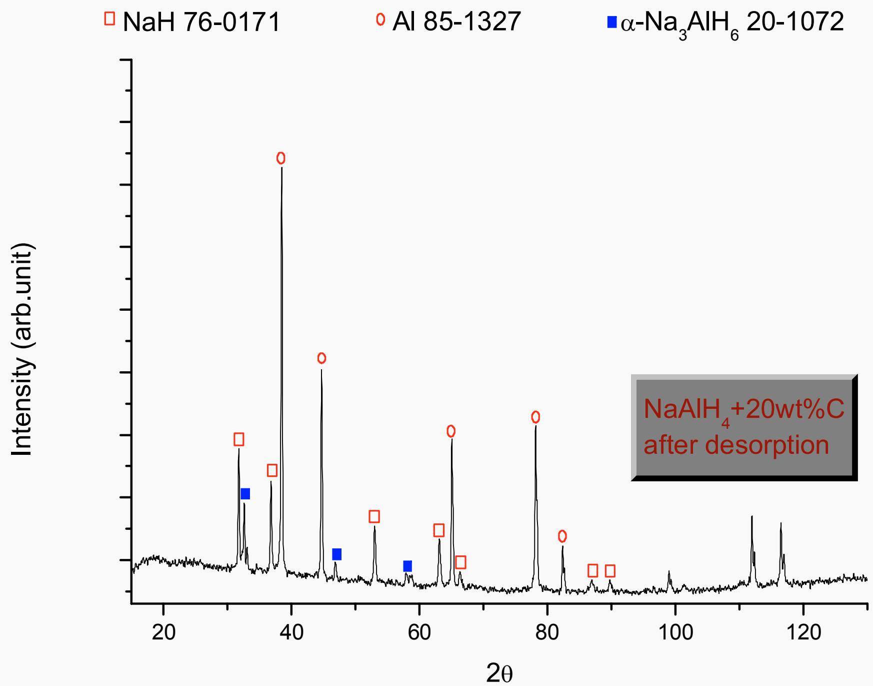


Crystal structure modifications



$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2$$



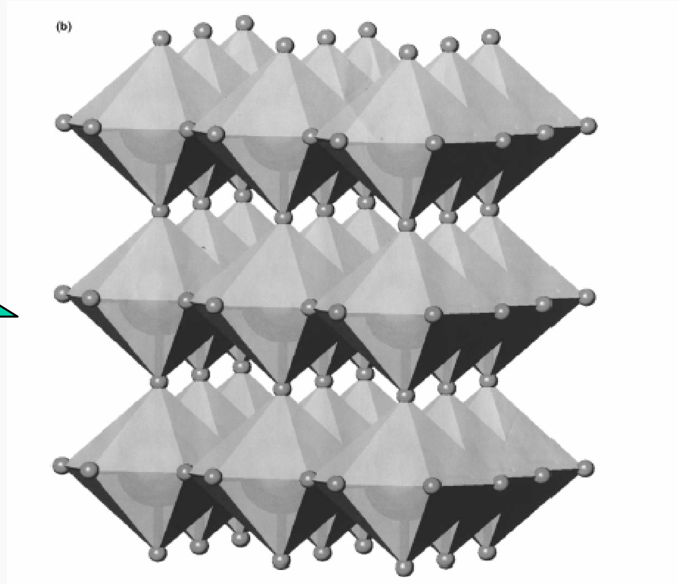
ENEA LONG TERM ACTIVITIES (2008): Li_3N

$Li_3N + H_2 \rightarrow LiH + Li_2NH$ 5.7 wt.% H_2

*$Li_2NH + H_2 \rightarrow LiH + LiNH_2$ 5.5 wt.% H_2

Li_3N is a red-brown powder

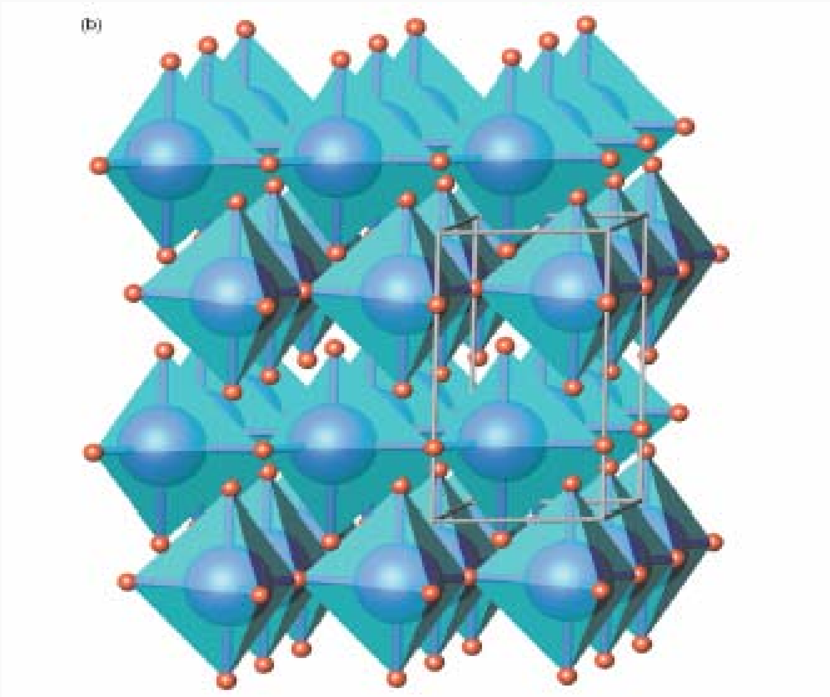
Crystal structure of Li_3N



*** P. Chen et al., Nature, vol. 420, 21 November 2002.**

THE β-Li_3N

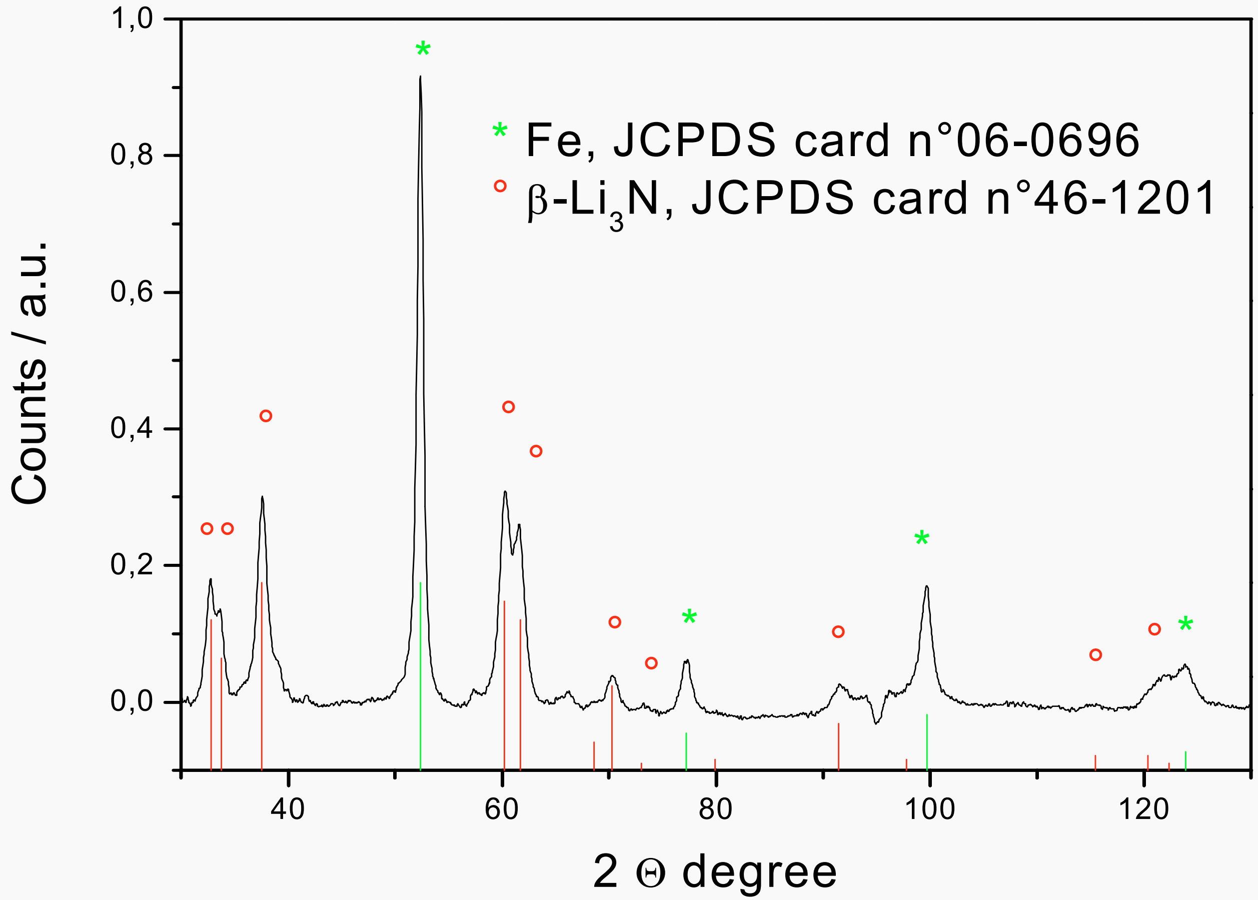
- A high-pressure form of Li_3N, called beta-Li_3N, is also known to exist.



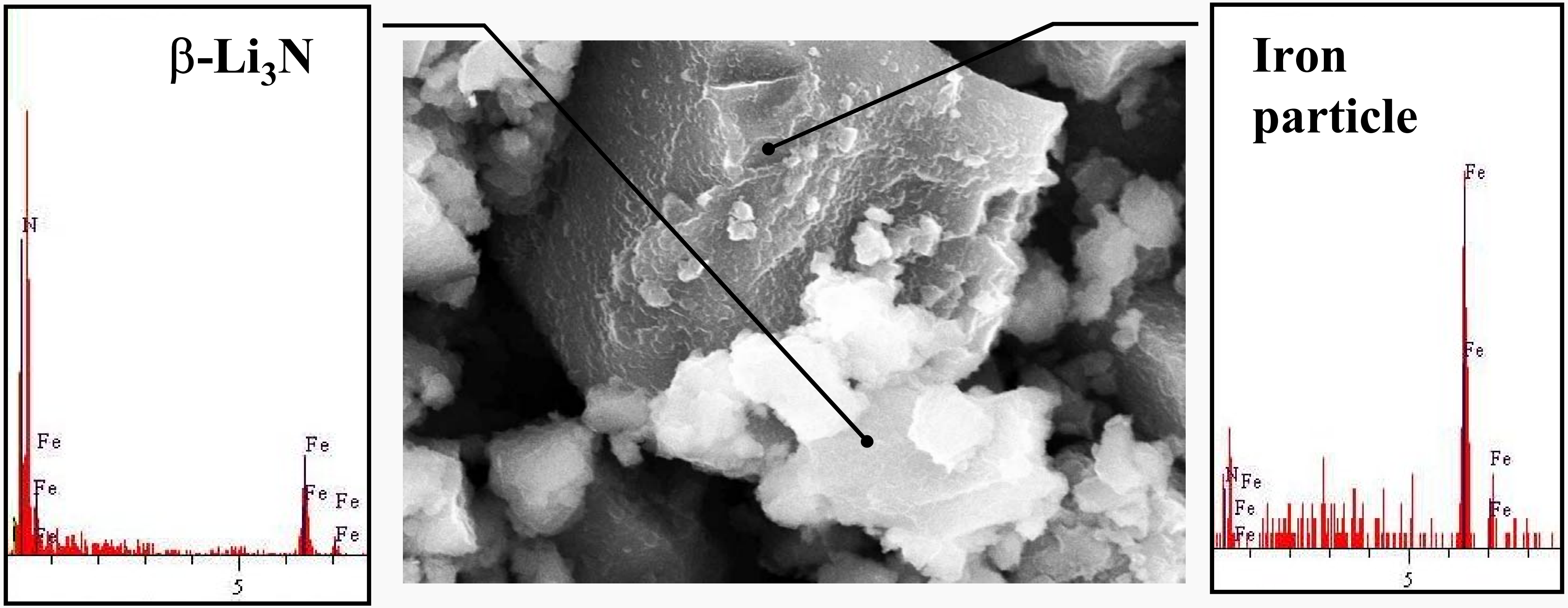
β-Li_3N is a black powder

We found that high energy ball milling in presence of iron is effective to transform α-Li_3N into β-Li_3N.

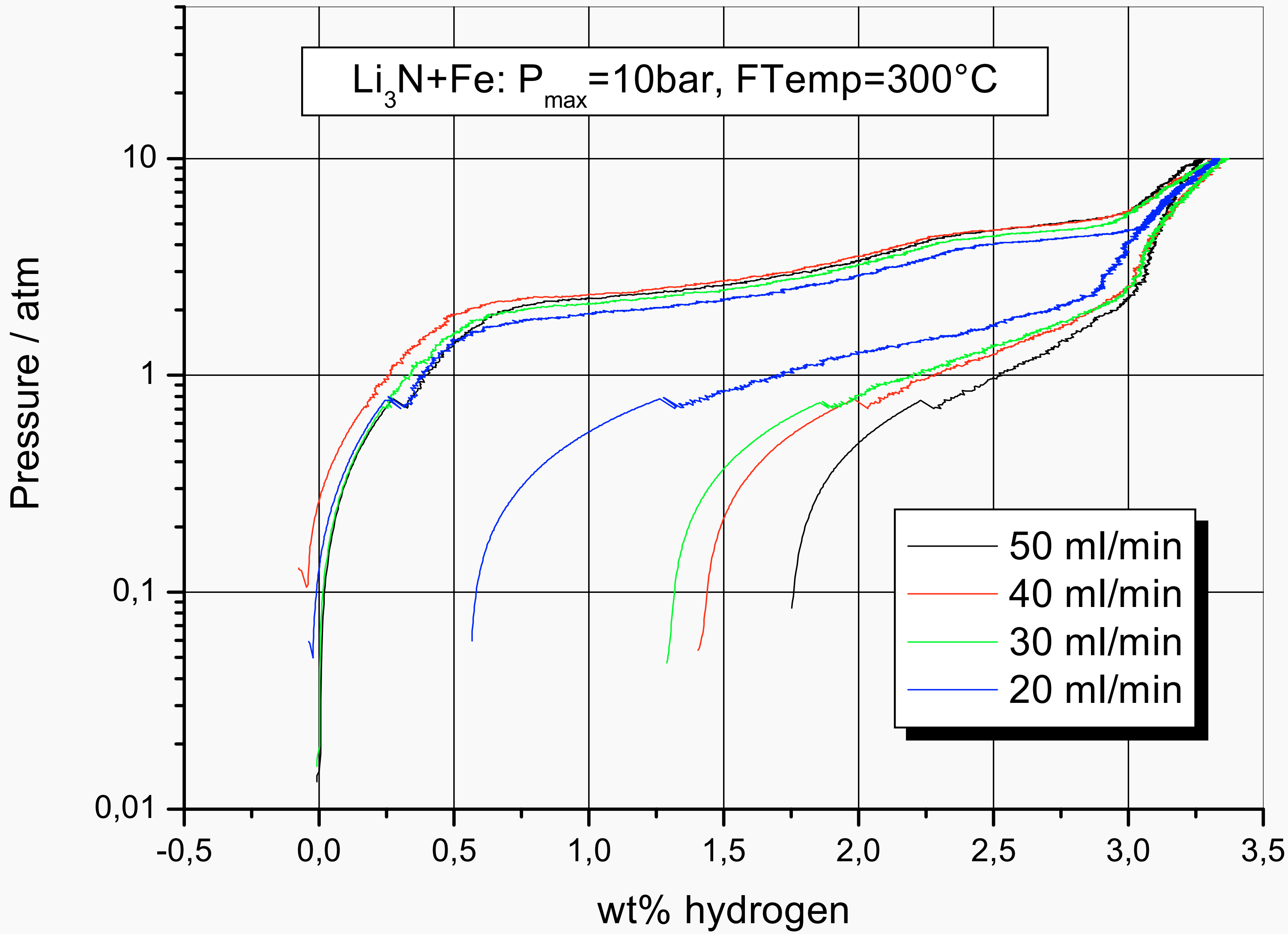
β-Li_3N was identified by XRD



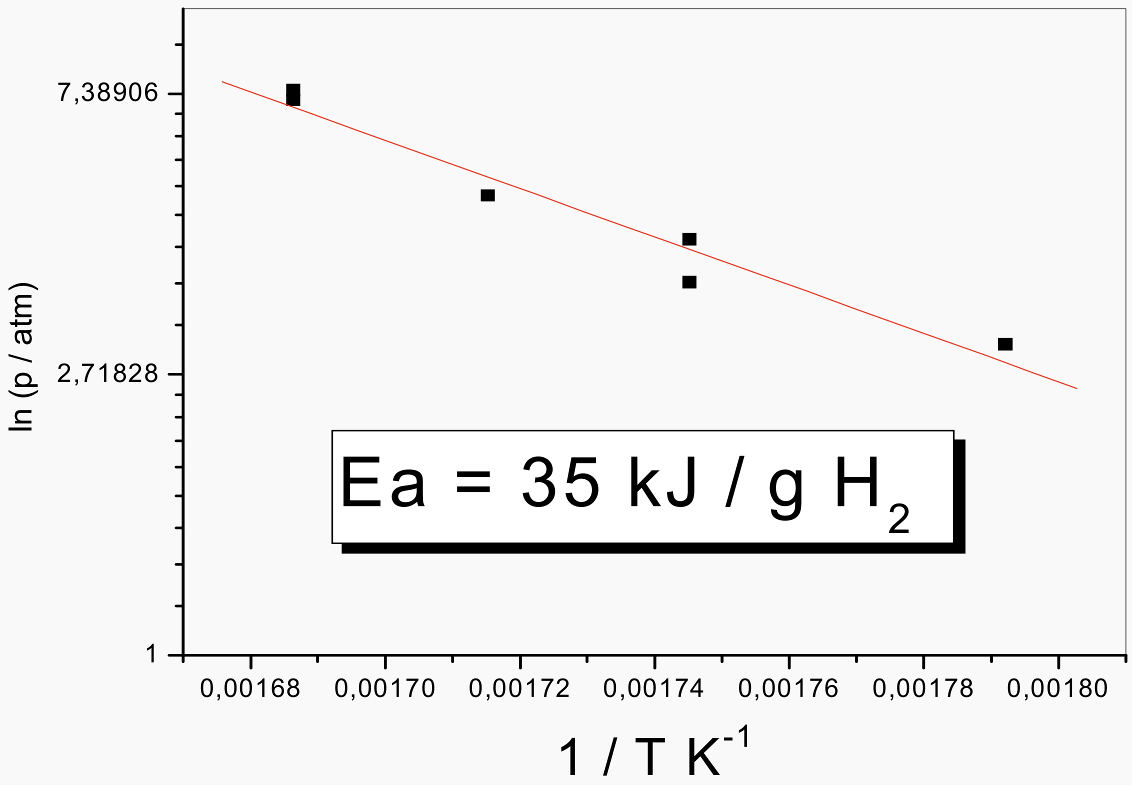
SEM and EDS analysis



PCI TEST FOR Fe MILLED Li_3N



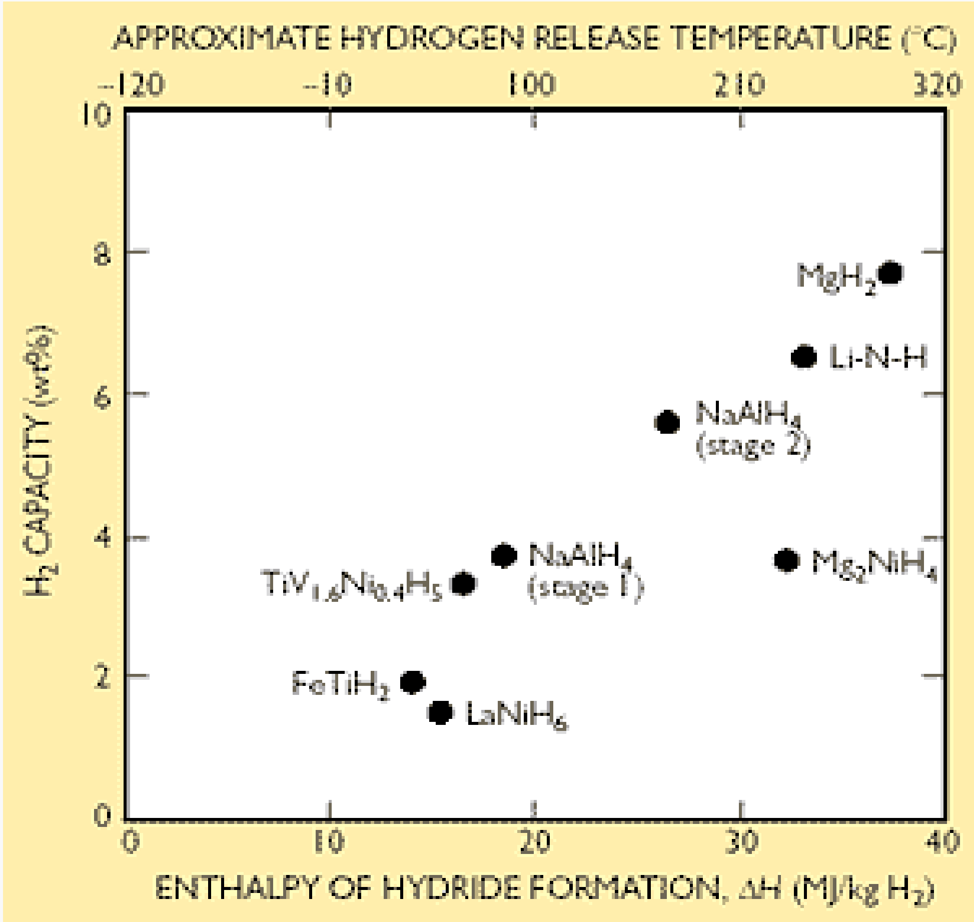
The enthalpy of reaction is 35 kJ per g H_2



The high enthalpy has several important consequences

- Working temperature is relatively high (285°C)
- Part of the hydrogen has to be "burned" to provide the heat for hydrogen desorbtion.

- This parasitic reaction can reduce the hydrogen content to about 70% of the stored one.



High enthalpy strongly increases the fill time.

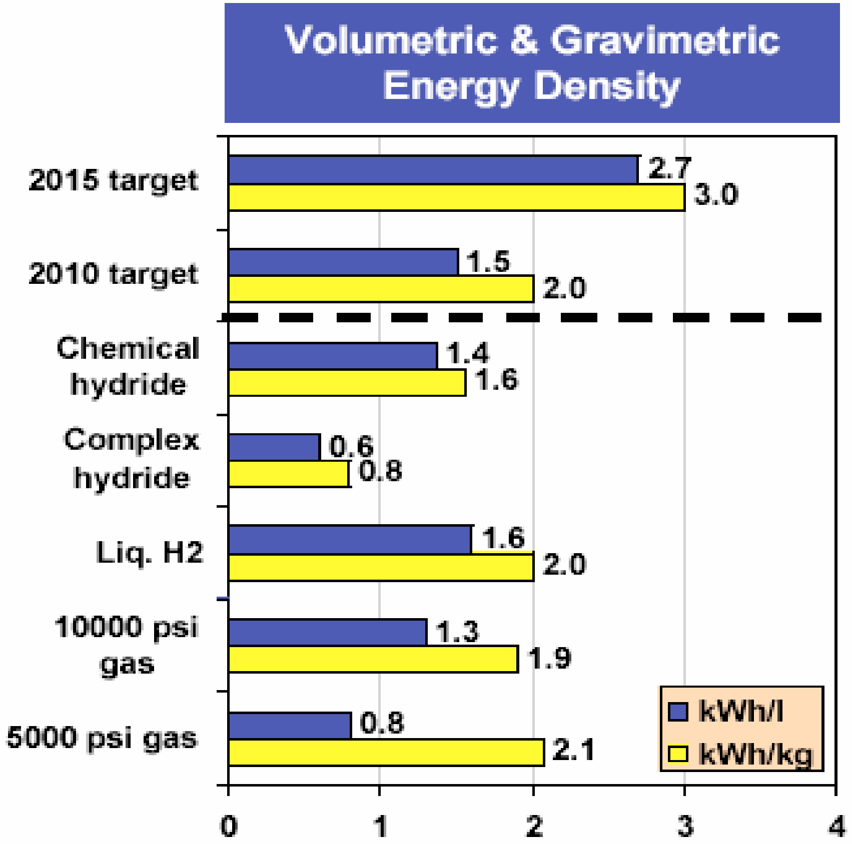
- Technological challenges are the fabrication of high temperature tanks able to exchange heat quickly.
- About 1 MW of heat should be disposed in a 2.5 minutes fast refill.

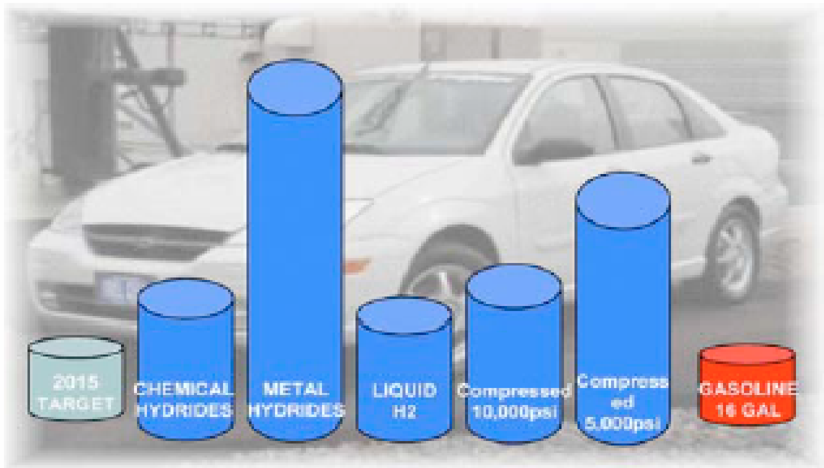
Heat exchanger

Car re-fuelling

Technology status

No current H_2 storage technology meets the 2015 targets.





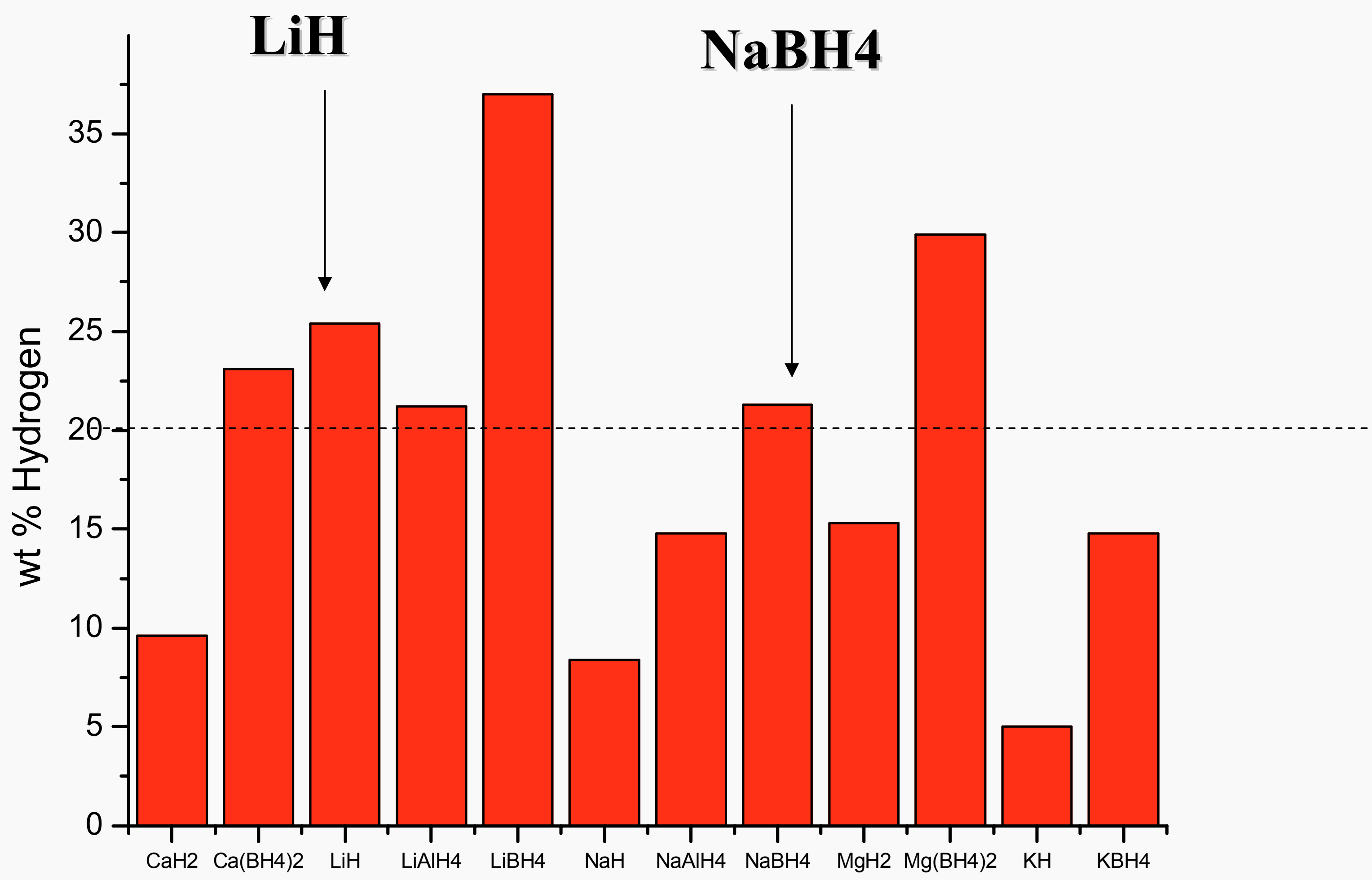
ANOTHER APPROACH
The hydrolysis of hydrides

- Reaction of some hydrides with water can represent an affordable method to produce hydrogen.

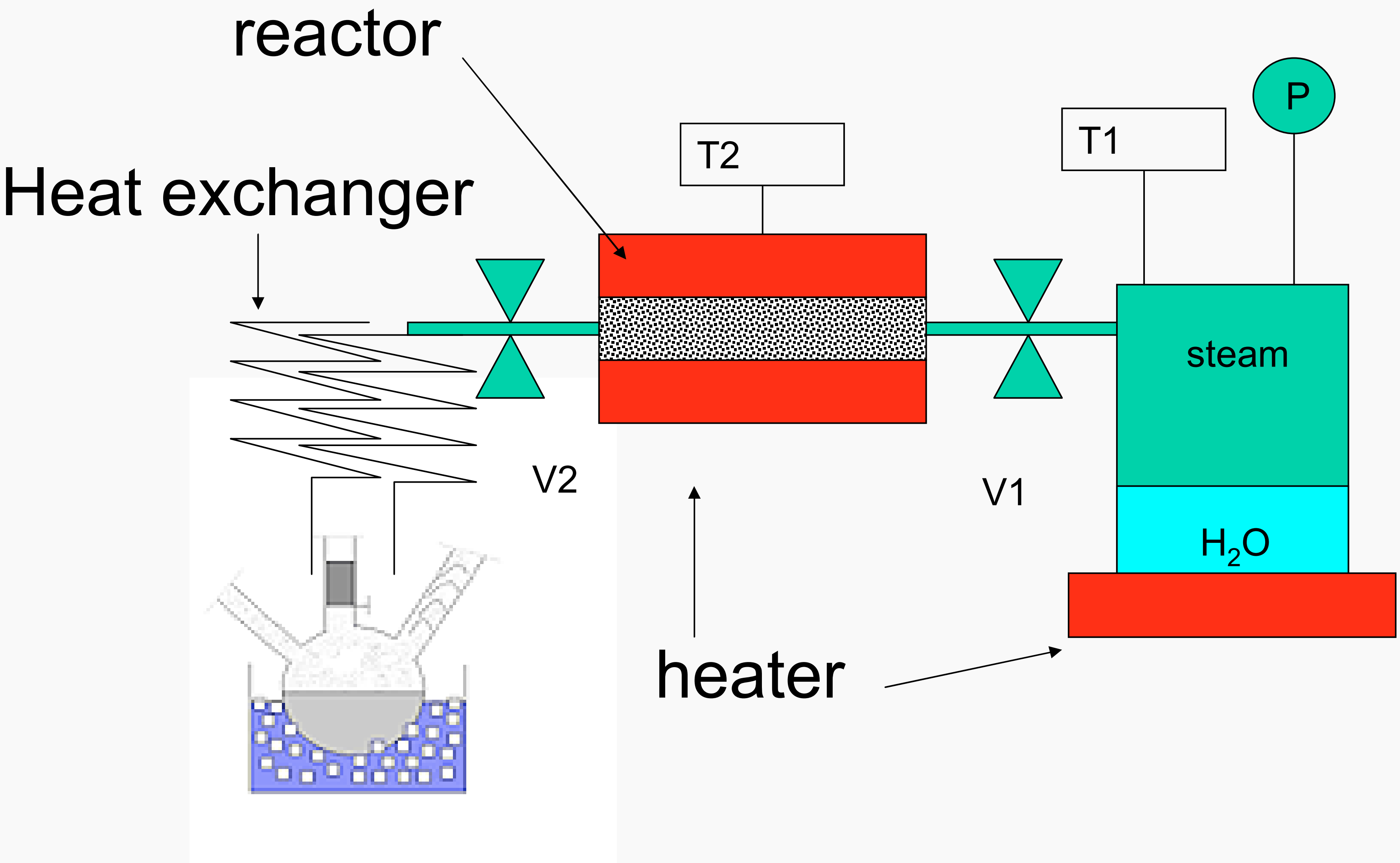
$$2\ MeH_n + n\ H_2O \rightarrow Me_2O + 2H_2$$

- The hydride must be regenerated off-board
- Considering fuel cell water recycling, the gravimetric energy density is very impressive!

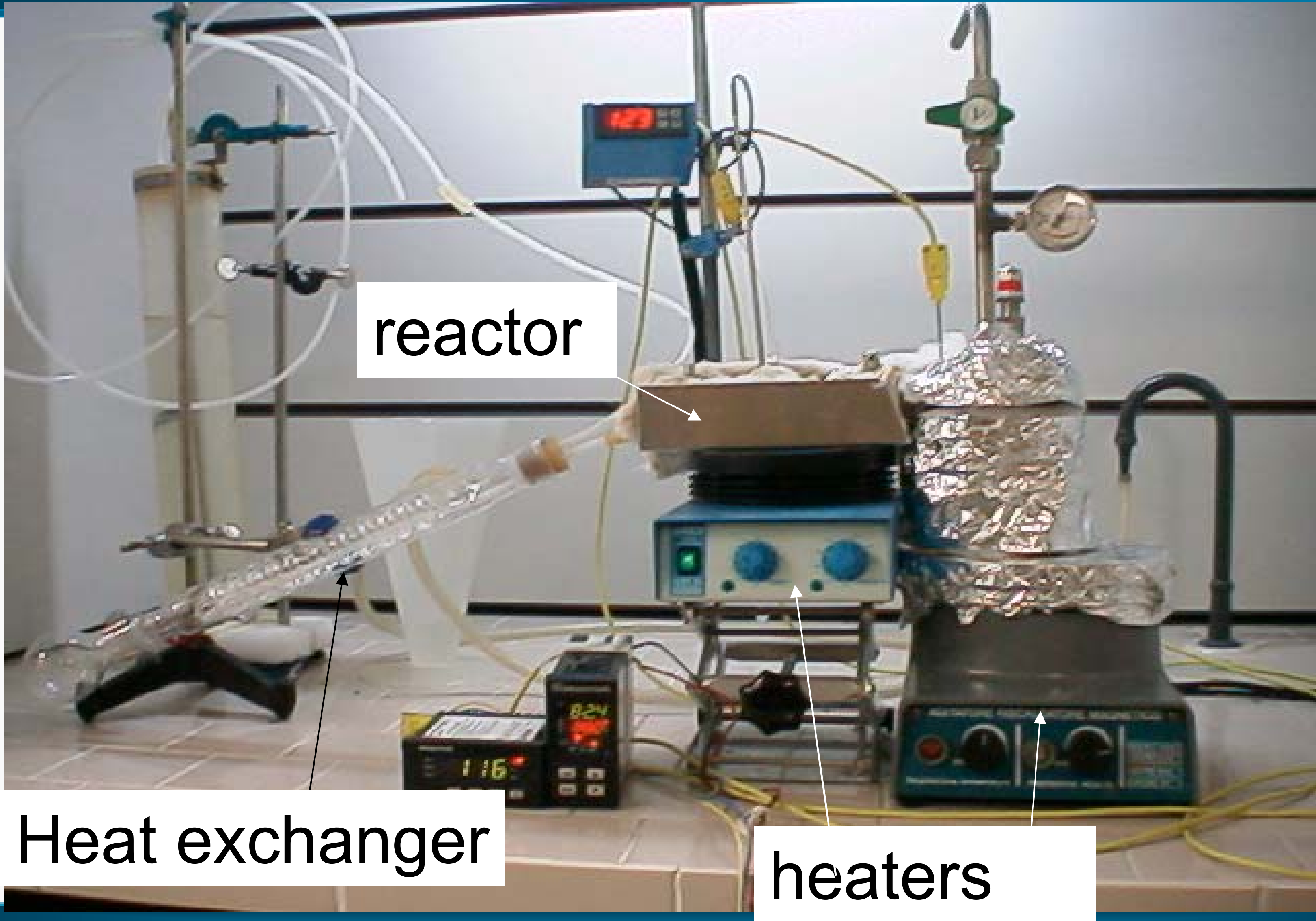
Among others, $NaBH_4$ and LiH have a theoretical hydrogen content higher than 20 wt. %



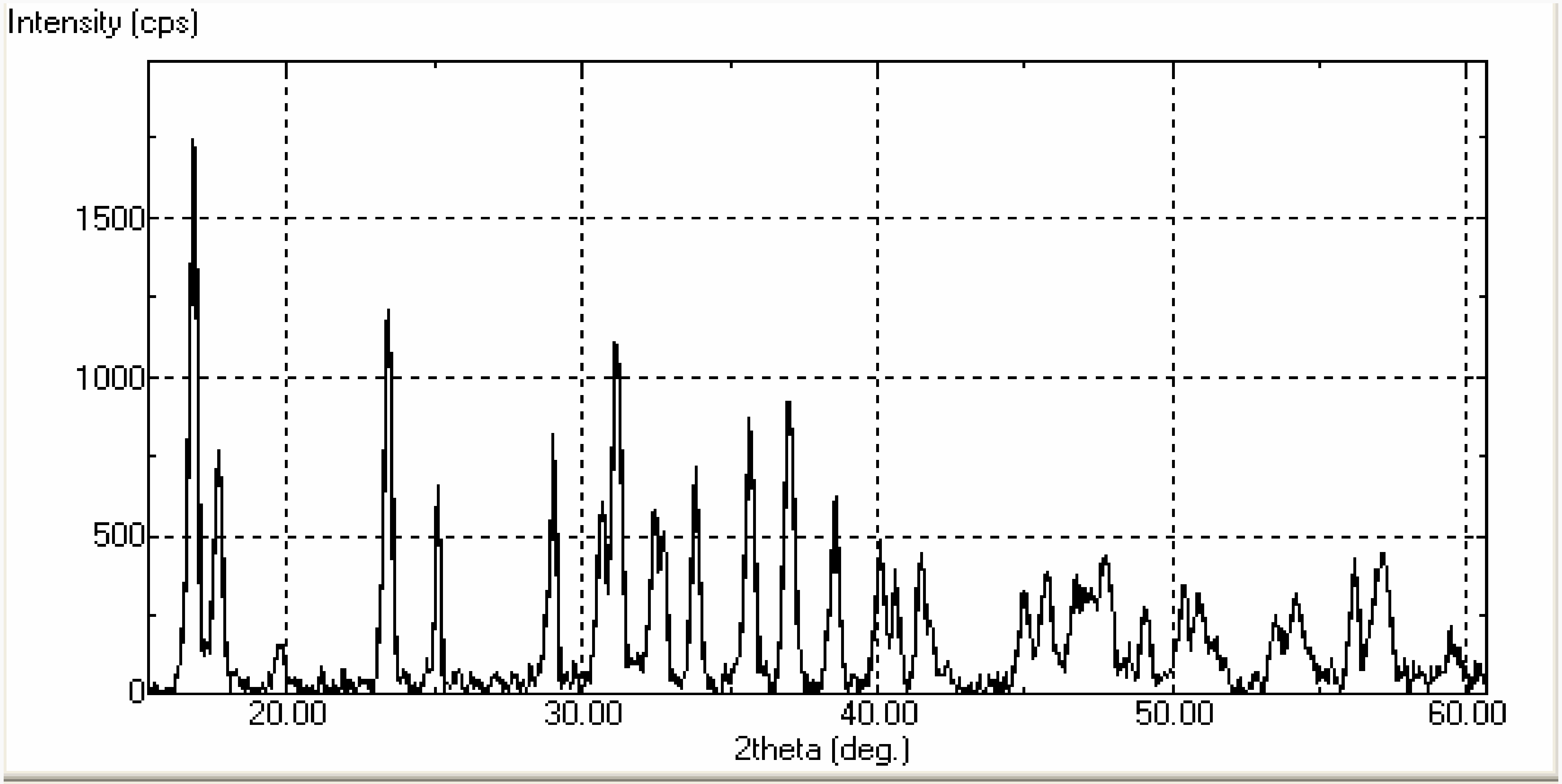
THE STEAM HYDROLISISOF HYDRIDES



Set up for hydride hydrolysis



$NaBH_4 + 3H_2O_{vap.} \rightarrow NaBO_2 \cdot H_2O + 4\ H_2$ @90°C



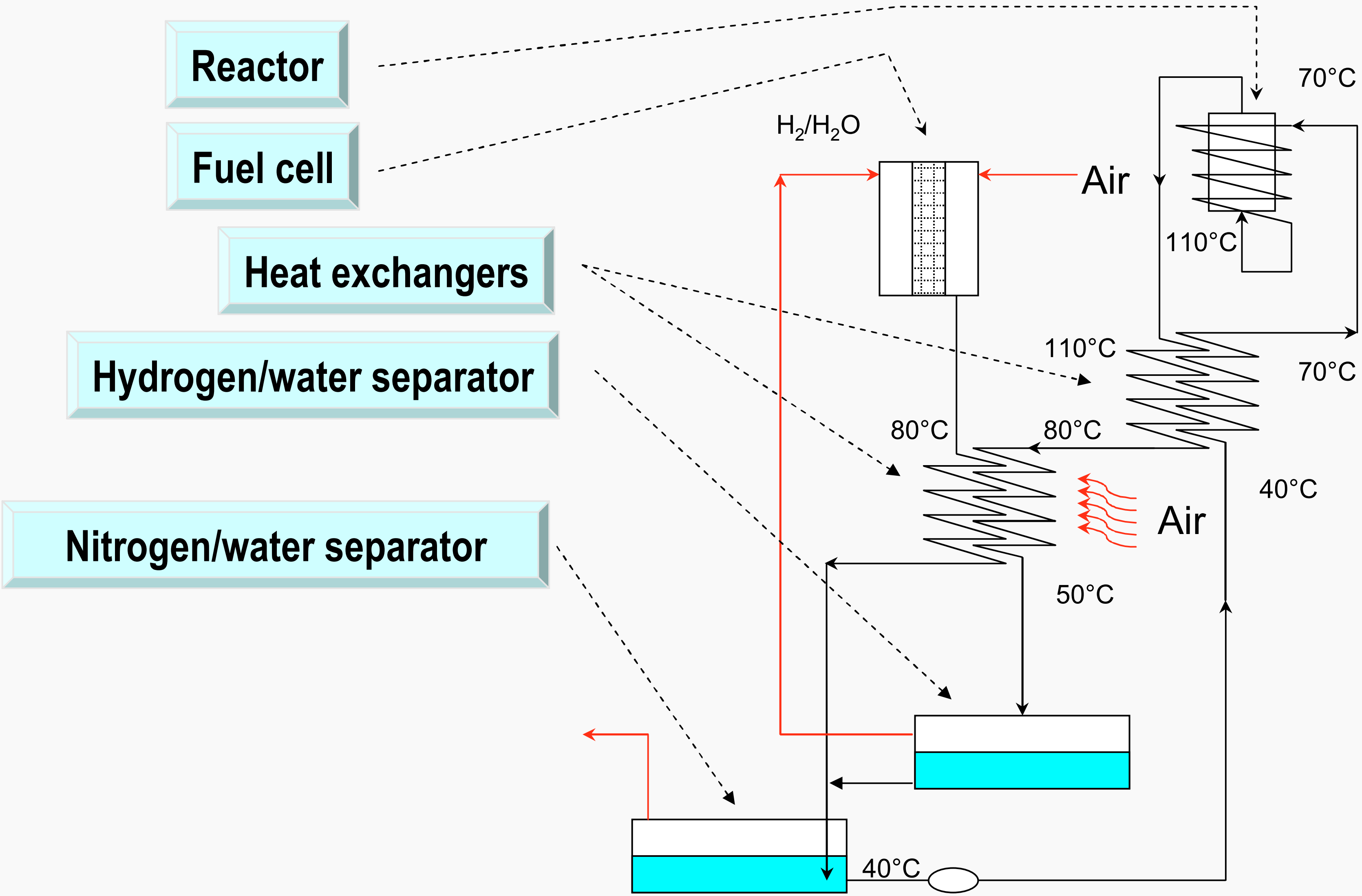
PROBLEMS THAT SHOULD BE SOLVED

- The reaction products occupy a volume larger than the parent material thus occluding the reactor and causing system failure.
- The reaction enthalpy for hydrolysis is very high and heat management is required.

in addition:

- A mixture of hydrogen and steam is delivered at high temperature and it has to be cooled before feeding the fuel cell.
- The condensed water has to be recycled into the reactor.
- The exchanged heat has to be used to produce steam

Schematic view of the complete system



The major problem is the cost

Today, the cost of $NaBH_4$ is about 30 €/kg (for 50 ton batch) but lower prices are expected for large scale production.

Since the cost of the raw materials is very low, the $NaBH_4$ production cost of is strictly related to that of electricity.

To reduce the cost both sodium production and hydride synthesis should be improved.

"Got any gas money ?"

Na metal from molten NaOH

Reaction Medium	Molten NaCl	Molten NaOH
Operating Temperature	600ºC	350ºC
Anode Product	Chlorine (Cl_2)	Water (H_2O)
Theoretical voltage	3.42 V	1.07 V
Actual voltage	~ 5.5 V	~1.2 V
Separator	Porous ceramic membrane	Selective sodium ion conducting ceramic membrane

Ying Wu et al., **Millennium Cell Inc., FY2004 Progress Report**

Development of new $NaBH_4$ production process

$NaBH_4$ can be regenerated from borax using MgH_2

* $Na_2B_4O_7 + 4MgH_2 \rightarrow 2NaBH_4 + 4MgO + B_2O_3$

The use of other low cost reducing agent could decrease the $NaBH_4$ cost.

Magnesium = 20 €/kg

Aluminum = 15 €/kg

Renewable ?????

* S. Suda et al. **Journal of Alloys and Compounds 349 (2003) 232–236**

To move toward a hydrogen-based economy some technological challenges have to be overcome.

- Light weight-high temperature-high pressure metal hydride are not suitable to be immediately introduced into the market
- Sodium boron hydride represent one of the most interesting candidate to efficiently store hydrogen.
- Parallel to technological improvements a new cultural model has to be developed.

“At the moment, only revisiting our style of life it will be possible to contribute to a cleaner environment.”

Portable hyDrogen Generator (PDG) TECHNICAL TARGET

The study was focused to the fabrication of a hydrogen generator for cellular phones and laptops.

Energy 30 Wh,
Power from 5 up 10 W

Energy 2 Wh, Power from 1 up 2 W

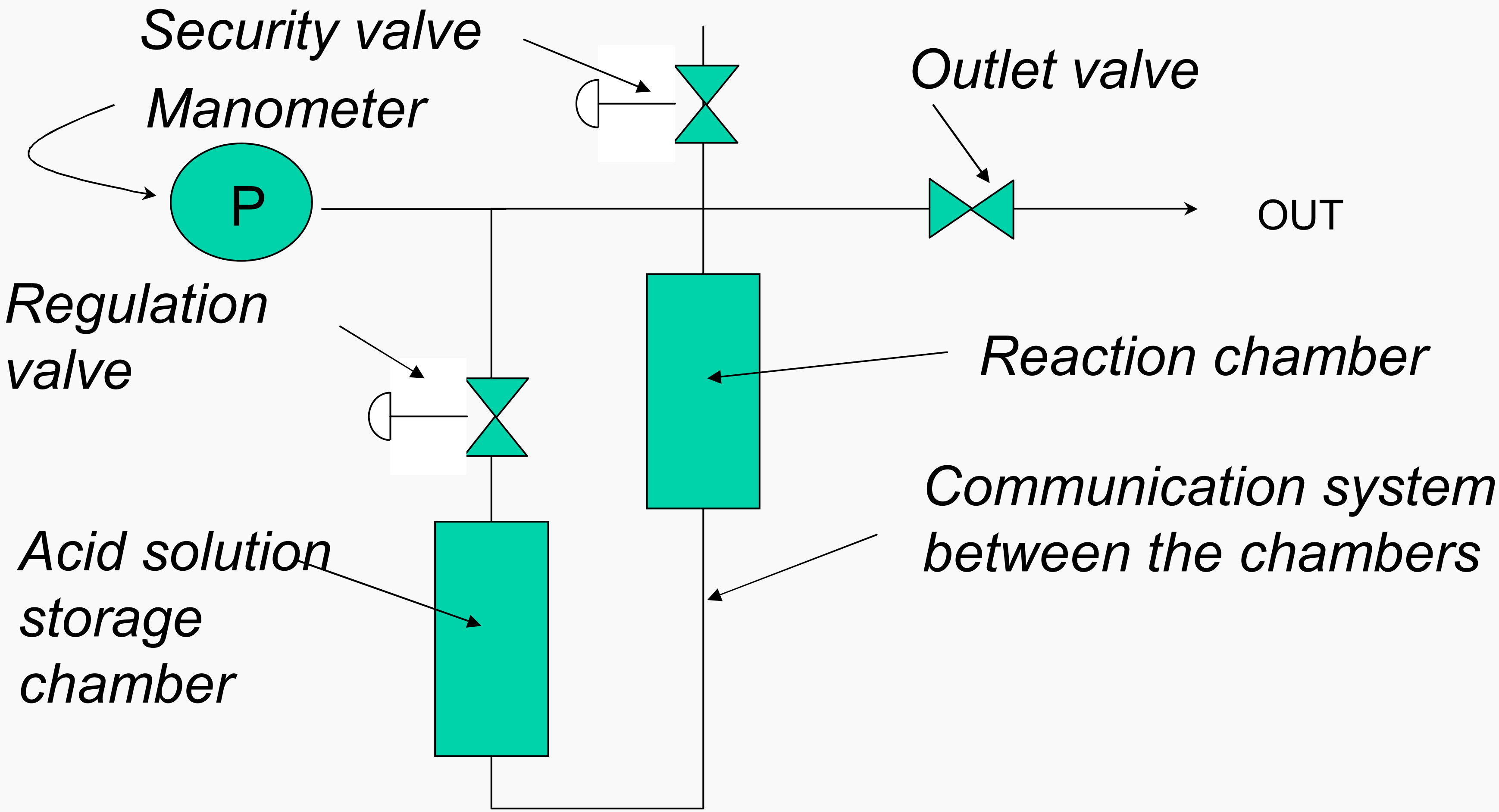
THE BASIC REACTION

ACID CATALYZED HYDROLISIS OF $NaBH_4$

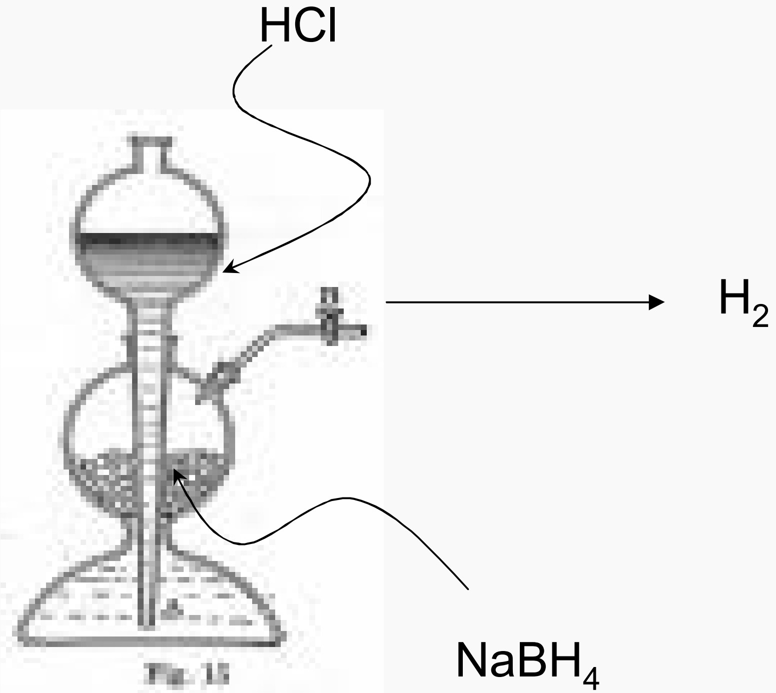
$$NaBH_4 + 7\,H_2O + HCl \longrightarrow NaCl + H_3BO_3 \cdot 4\,H_2O + 4\,H_2 \qquad (1)$$

Based on reaction (1) the hydrogen content is about 4.0 % wt.

SCHEMATIC VIEW OF PDG



THE BASIC MECHANISM: THE KIPP APPARATUS (1808-1864)



PDG DESIGN

Regulation valve

Activation system

$NaBH_4$

Diaphragm

Reaction chamber

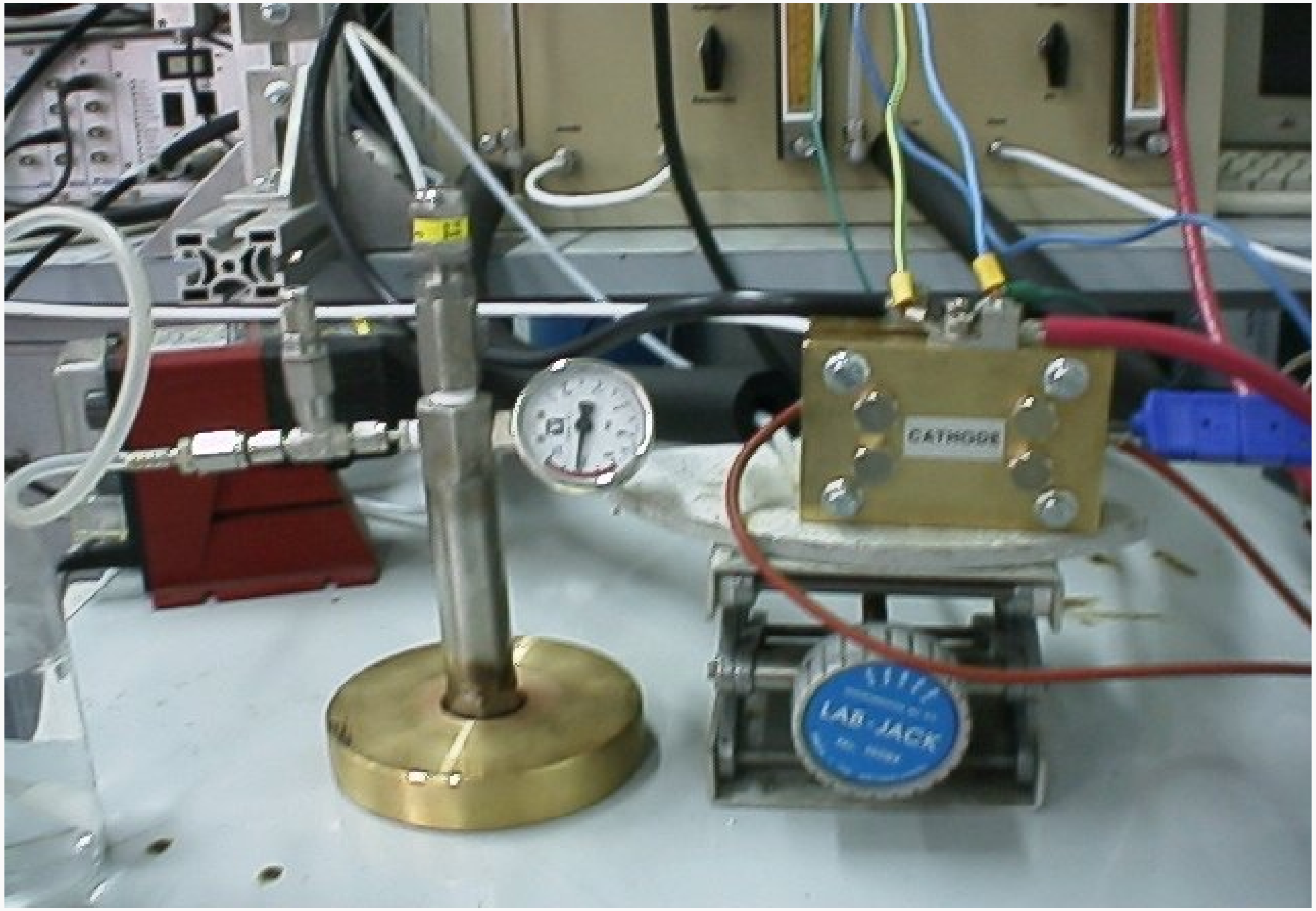
Filter

Channel of communication between the chambers

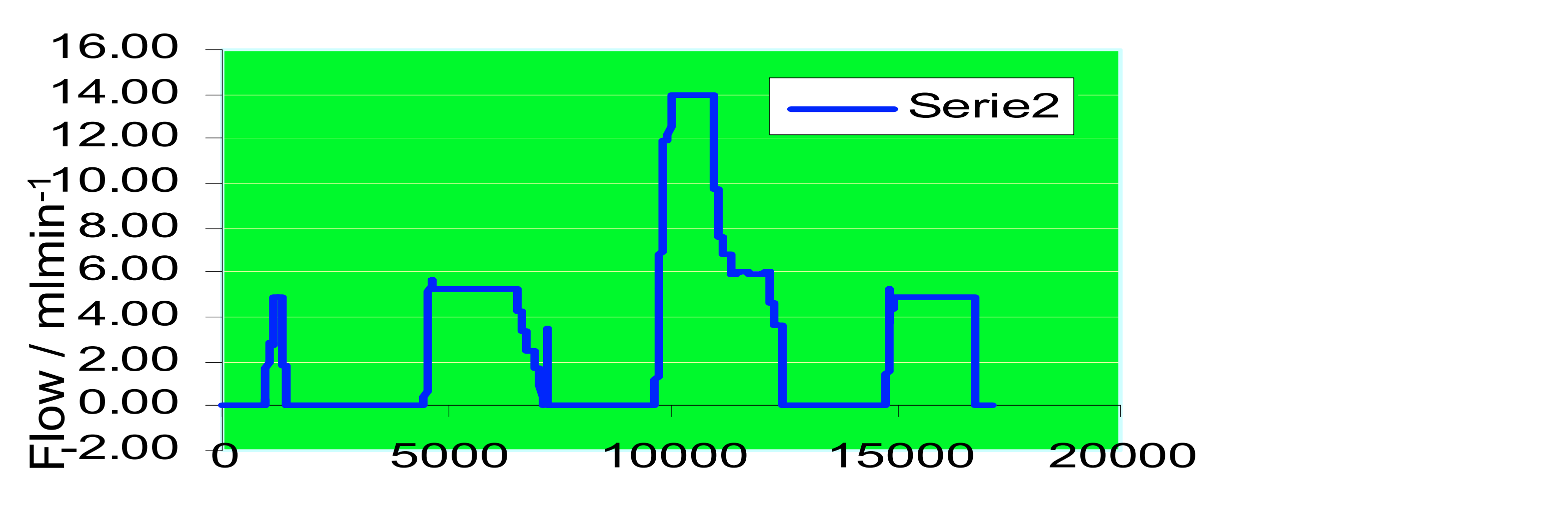
Acid solution chamber

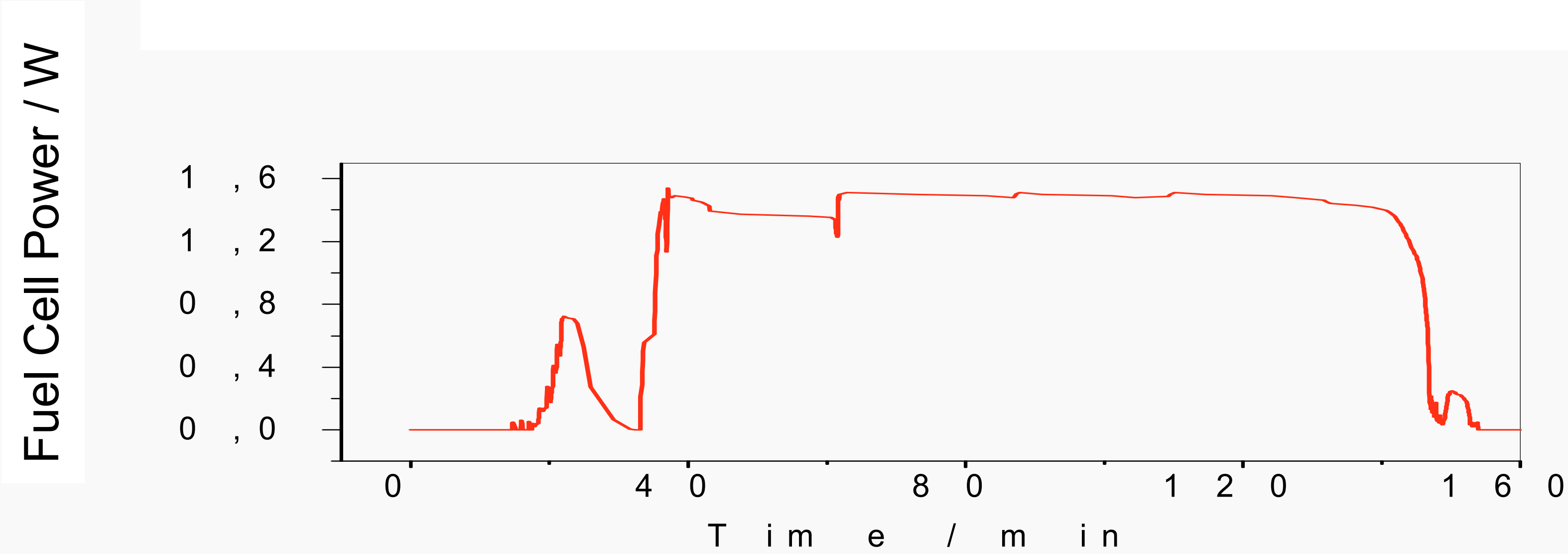
PDG ACTIVATION

THE SYSTEM WAS COUPLED WITH A FUEL CELL

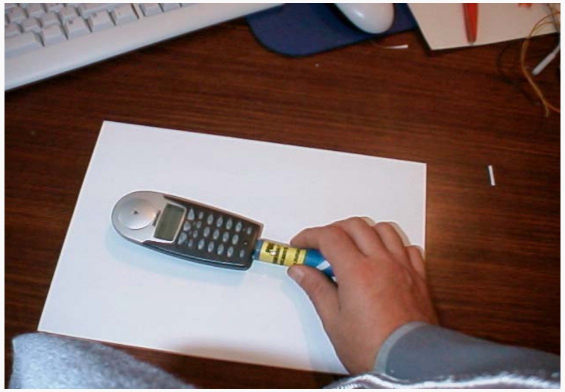


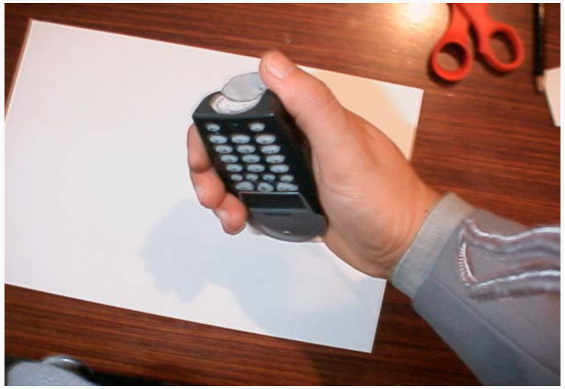
PDG WAS DEMONSTRATED ABLE TO POWER CELLULAR PHONE

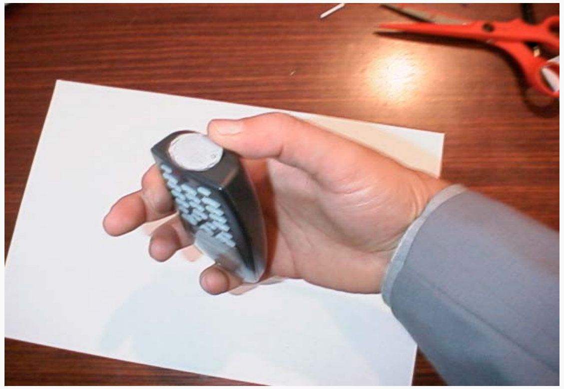




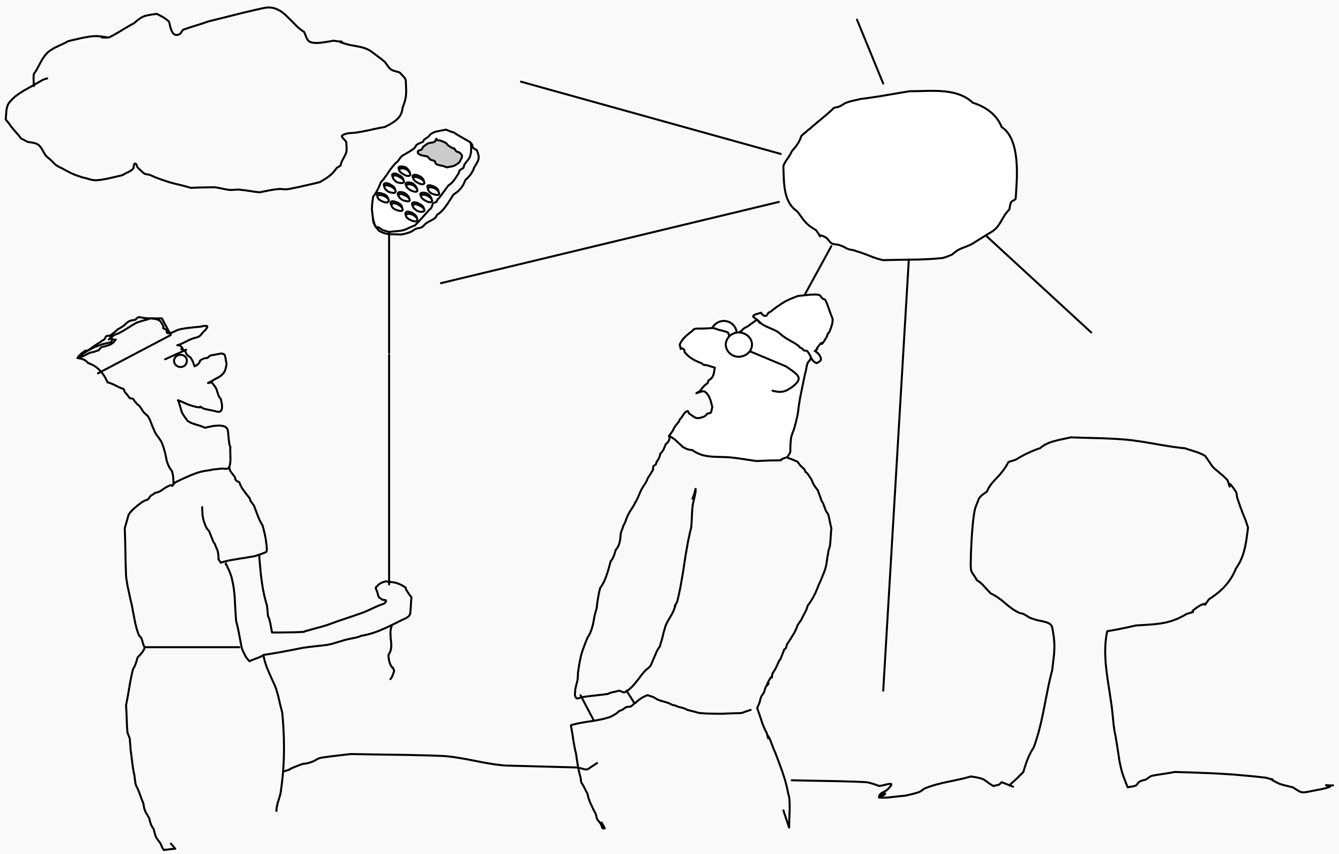
IT WILL BE POSSIBLE?







TANK YOU FOR YOUR ATTENTION



"It works on hydrogen"